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16. Abstract (MAXIMUM 200 WORDS)

The assessment of compliance by ships with mandatory ballast water exchange (BWE) is limited by the difficulty of verifying whether BWE was implemented. Previous research indicates that concentrations in ballast water of barium, phosphorous and manganese and chromophoric dissolved organic matter (CDOM) can be robust tracers of BWE. The current study examined the seasonal and spatial variability of BWE tracers in Pacific rim ports and the adjacent seas, using the north Pacific as a model system to examine whether it would be possible to set universal thresholds for tracer concentrations in ballast water that can consistently and effectively discriminate tanks that have undergone BWE from tanks that have not. Surveys were conducted in eight port systems in North America and Asia and along perpendicular and coastwise transects off the US Pacific coast. CDOM decreased rapidly with increasing distance from land, whereas barium, phosphorous, and manganese exhibited more seasonally and regionally variable trends. CDOM tracers could usually discriminate between port (<0.2 nautical miles (nmi) from land) and oceanic samples, but not necessarily between BWE performed in coastal (0.2nmi to 100 nmi from land) versus oceanic (>100nmi from land) locations. This result has important implications for verifying BWE performed according to state legislation, which allows BWE as close as 50 nautical miles from land.

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EXECUTIVE SUMMARY

The role played by ships' ballast water in delivering non-native organisms to coastal marine systems in North America is well known (Fofonoff et al., 2003; Ruiz and Carlton, 2003). To reduce the risk of invasions, ships arriving from overseas are required to treat ballast water before discharge in U.S. waters. In addition, ships arriving with water from U.S. ports are also required to treat this ballast before discharge at some locations. Several treatment options are being developed and examined. Currently, open ocean ballast water exchange (BWE) is the only treatment that is approved and readily available to vessels to meet regulations for mandatory ballast water treatment. Methods to verify whether or not BWE has occurred are very coarse, limiting assessment of compliance with current Coast Guard regulations.

Direct measurement of naturally-occurring tracers in the ballast water offers a potentially powerful approach to BWE verification. The general approach is to deduce whether a tank was ballasted in a port or offshore location, based upon concentrations of chemical constituents that differ between these sources. Prior research conducted for U.S. Coast Guard identified five natural chemical tracers with potential for verifying BWE. They consisted of the trace elements (barium (Ba), phosphorous (P), and manganese (Mn)) and chromophoric dissolved organic matter (CDOM), with the latter measured via its fluorescence at the wavelength (λ) positions C2* (λ_{ex}/ λ_{em} 320/414 nanometers (nm)) and C3* (λ_{ex}/ λ_{em} 370/494 nm). The performance of these tracers was promising based upon demonstration of a consistent detectable difference between tracer concentrations in ballast water of coastal versus oceanic origin, even in cases where salinity changes were negligible (Murphy et al., 2006; 2008; submitted).

The current study examined the seasonal and spatial variability of BWE tracers in Pacific rim ports and the adjacent seas in order to determine whether the implementation of BWE according to specified guidelines would result in predictable concentrations in ballast tanks that differ from ranges in ports. This is a more robust examination of tracer utility than past studies, using the north Pacific as a model system to examine whether it would be possible to set universal thresholds for tracer concentrations in ballast water (given observed levels of spatial and temporal variation) to consistently and effectively discriminate tanks that have undergone BWE from tanks that have not.

This report presents the results of extensive surveys carried out in eight port systems in North America and Asia, together with a large number of offshore sites sampled along perpendicular and coastwise transects. The resulting dataset of more than 2,500 samples across sites and seasons provides the most comprehensive picture to date of the relationship between BWE tracer concentrations and distance from land. The data show that all five tracers are spatially and temporally variable. Despite this, CDOM concentrations showed strong decreases between ports and open ocean, generally occurring rapidly with distance from land. In contrast, Ba, P and Mn either exhibited inconsistent trends or else the effect of proximity from land was masked by large seasonal and regional variations in their oceanic concentrations.

This study shows that CDOM tracers can discriminate between oceanic samples and the vast majority of samples obtained from within ports and embayments less 0.2 nautical miles (nmi) from shore. However, due to its rapid decrease within short distances from land, it would in many instances provide insufficient sensitivity to determine whether ships have performed BWE in the open ocean versus in coastal waters.

Selection of the offshore boundary for BWE is shown to be critical to the success of natural tracer methods for verifying BWE. Whereas CDOM concentrations in oceanic waters farther than 100 nmi from land were substantially lower than observed in ports, CDOM between 50 to 100 nmi from land was elevated in northern latitudes adjacent to the U.S. and Canada. This resulted in significant (10–20 percent) overlap between CDOM concentrations in port samples versus the most concentrated samples from the ocean in these regions. This result has important implications for verifying BWE performed according to state legislation, which allows BWE as close as 50 nmi from land (CSLC, 2006; DEQ, 2001; WDFW, 2007). It is recommended that further analysis formally examine the effects of specific threshold concentrations and offshore distances in the application of CDOM concentration for BWE verification.

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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

Tracers		
Ba	Total dissolved barium	μgL^{-1}
C2*	CDOM peak C2* ($\lambda_{ex}/\lambda_{em}$ = 320/414 nm)	QSE
C3*	CDOM peak C3* ($\lambda_{ex}/\lambda_{em}$ = 370/494 nm)	QSE
CDOM	Chromophoric dissolved organic matter	QSE
Mn	Total dissolved manganese	μgL^{-1}
Mo	Total dissolved molybdenum	μgL^{-1}
P	Total dissolved phosphorus	μgL^{-1}
λ_{ex}, λ_{em}	Wavelengths of excitation, emission	nm
Measures and Units		
A	Absorbance	
˚C	Degrees Celsius	
cm	Centimeter	
g	Gram	
L	Liter	
m	Meter	
M^3	Cubic meters	
MT	Metric tons	
N	Normal	
nm	Nanometers (10^{-9} m)	
nmi	Nautical miles (= 1852 m precisely)	
ppb	Parts per billion	
psu	Practical salinity units	
μgL^{-1}	Micrograms per liter	
Port Surveys		
HK	Hong Kong, China	
JP	Tokyo Bay, Japan	
KR	Busan, Korea	
PS	Puget Sound	
SFB	San Francisco Bay	
SG	Strait of Georgia	
SJF	Strait of Juan de Fuca	
TW	Kaohsiung, Taiwan	
Other Acronyms		
BC	Province of British Columbia, Canada	
BWE	Mid-ocean ballast water exchange	
CA	State of California, USA	
CAN	Canada	
CDF	Cumulative density function	
CLSC	California State Land Commission	
CTD	Conductivity / Temperature / Depth sensor	
EEM	Excitation emission data matrix	
EEMS	Excitation emission matrix spectroscopy	
EEZ	Exclusive economic zone	
GPS	Global Positioning System	
HC1	Hydrochloric acid	
HNO_3	Nitric acid	

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS (continued)

Other Acronyms (continued)

ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IFE	Inner filter effects
IMO	International Maritime Organization
NOAA	National Ocean and Atmospheric Administration
QA/QC	Quality Assurance/Quality Control
QSE	Quinine sulfate equivalent
PDF	Probability density function
pH	Potential of Hydrogen
R/V	Research Vessel
SERC	Smithsonian Environmental Research Center
USA	United States of America
WA	State of Washington, USA

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1 INTRODUCTION

The incidence of species invasions has increased with the global expansion of commerce, particularly involving marine transportation. Most international trade occurs by commercial shipping. Although living organisms are sometimes intentionally transported in trade, such as commercial crops and ornamental plants, many other organisms are transported unintentionally across historical dispersal barriers and establish self-sustaining, introduced populations. The rate of such biological invasions appears to have increased dramatically in recent time (Ruiz et al., 2000), causing significant concerns about the ecological, economic, and conservation impacts.

In coastal ecosystems, biological invasions are illustrated by the introduction of the zebra mussel to the Laurentian Great Lakes from Europe. This mollusc is thought to have been introduced unintentionally to the Great Lakes through ballast water discharged by one or more commercial ships. Once established, the mussel has spread rapidly throughout much of the central United States and has recently been found on the West Coast. The mussel has had serious ecological and economic consequences, including a financial burden related primarily to power plant and municipal water supply maintenance (Pimentel, 2005).

The global dispersal of aquatic organisms in ships' ballast water and attached to hulls is responsible for many documented invasions by non-native species (Cranfield et al., 1998; Fofonoff et al., 2003; Hewitt et al., 2004; Hewitt et al., 1999; Ruiz et al., 2000). As a result, management and policy responses at local, national, and international levels have focused on reducing the risk of ship-mediated invasions (Ruiz and Carlton, 2003). To date, ballast water management has received the majority of this attention. This has resulted in guidelines, state and federal regulations (CSLC, 2006; USCG, 2004), and an international convention (pending ratification) for the management of ships' ballast water (IMO, 2004).

In the U.S., federal regulations require that ships arriving from outside of the exclusive economic zone (EEZ) conduct ballast water exchange (BWE) at 200 nautical miles (nmi) from shore, prior to ballast discharge in coastal waters (USCG, 2004). The states of California, Oregon, and Washington also require coastwise, domestic traffic (when crossing particular regional boundaries) to conduct BWE 50 nautical miles (nmi) from shore before discharge into state waters (CSLC, 2006; DEQ, 2001; WDFW, 2007).

To conduct BWE, tanks that are filled with water from a port or another coastal source are flushed out in open ocean during transit. This treatment is intended to reduce the concentrations of coastal organisms that pose a risk of invasions upon discharge at other ports or coastal areas. Although various ballast water treatments are being advanced, BWE is currently the only approved treatment method available for routine use by commercial ships. BWE is likely to be in use by some ships for at least the next decade, as new treatment technologies are being implemented.

Despite existing regulations at the state and federal levels in the United States, reliable techniques are lacking to verify whether ballast tanks have undergone BWE. At the present time, a combination of shipboard records and salinity are used to assess compliance. However, salinity cannot discriminate water collected from open ocean measurements versus high salinity ports, leaving uncertainty about whether BWE has occurred. Since high salinity ports are common throughout the world, this method of BWE verification is clearly limited.

Recent research at the Smithsonian Environmental Research Center (SERC) has identified naturally occurring organic and inorganic seawater constituents that appear to discriminate between open ocean and coastal sources of water. One of these, chromophoric (or colored) dissolved organic matter (CDOM) is the optically active fraction of dissolved organic carbon that occurs naturally in fresh and marine waters, and absorbs visible as well as ultraviolet-A (315–400 nanometers (nm)) and ultraviolet-B (280–315 nm) light. CDOM affects absorption of sunlight in aquatic ecosystems, and consequently plays a major role in regulating the availability of sunlight for photosynthesis within the water column. Natural CDOM concentrations from lakes to the deep ocean arise from input via the breakdown and dissolution of terrestrial and marine vegetation (Kalle, 1966; Sieberth, 1969; Stabenau et al., 2004), microbial productivity in the water column (Nelson et al., 1998) and exchange with sediment porewaters (Burdige et al., 2004; Skoog et al., 1996), and removal due to bleaching by sunlight (Green and Blough, 1994). Other inputs affecting overall CDOM distribution include industrial effluents and agricultural and urban runoff (Bergamaschi et al., 2005).

In general, CDOM concentrations decrease greatly with increased distance from shore, moving from estuaries to open ocean. Since oceanic concentrations of CDOM are very low, high CDOM is potentially a good indicator of unexchanged ballast water from port and nearshore coastal sources. Moreover, fluorescence measurements of CDOM provide a sensitive proxy for monitoring concentrations, such that instrumentation can be modified for easy field use and real-time measurements aboard ship for ballast tank sampling.

Some trace elements also occur at much lower concentrations in surface oceanic waters than in coastal and port environments, and these may act as effective tracers of unexchanged ballast water. Since metals and many other elements are principally sourced from the earth's crust and anthropogenic activities, and removed in the deep ocean, their dissolved concentrations are typically highest in lakes, rivers and coastal environments. A large number of trace metals (e.g., iron, copper, nickel, and zinc) are present in highly elevated concentrations in coastal environments in comparison to the open ocean, but some are constituents of common materials used in and on ships (and therefore easily contaminated) and are challenging to measure accurately except under ultra-clean conditions. In contrast, a subset of trace elements have proved both useful indicators of terrestrial seawater and possible to measure accurately in ballast water, showing some promise for application to BWE verification.

CDOM and selected trace elements have each been used experimentally to discriminate between high salinity coastal and oceanic ballast water in multiple shipboard and ballast water measurements in the North Pacific and Atlantic oceans. Murphy et al. (2006) identified exchanged ballast water based on the fluorescence of CDOM measured for two wavelength (λ) positions: C2* (λ_{ex}/ λ_{em} 320/414 nm) and C3* (λ_{ex}/ λ_{em} 370/494 nm). In this work, upper thresholds for CDOM concentration in exchanged ballast tanks were estimated to be approximately 1.7 quinine sulfate equivalents (QSE) at C2* and 0.7 QSE at C3*. Concentrations exceeding either threshold indicated the ballast water retained significant coastal influence. The success rate using this method exceeded 95 percent for approximately 500 samples collected during nine cruises in the North Pacific and North Atlantic Oceans, indicating that these wavelength positions and their respective thresholds were promising chemical tracers of BWE.

Results for trace elements in parallel experiments indicated that concentrations of barium (Ba), phosphorus (P) and manganese (Mn) were significantly lower in tanks that had undergone BWE compared to untreated tanks (Murphy et al., 2004a; Murphy et al., 2008). In the Atlantic Ocean, unexchanged ballast tanks were identified by Ba concentrations exceeding 7 micrograms per liter (μgL^{-1}) and P concentrations exceeding 6

μgL^{-1}, whereas Ba and P concentrations in tanks exchanged in the Pacific were higher and more spatially variable (Murphy et al., 2008). Mn concentrations in tanks exchanged in the Pacific were more uniform, typically falling below 1 μgL^{-1}.

The current study seeks to evaluate overall performance of tracers across multiple port sources and seasons, using the North Pacific as a model system. In this study, the scope of earlier analyses was greatly expanded to include CDOM and trace element concentration measurements for (a) selected ports in the eastern and western Pacific, (b) different distances from shore, and (c) coastwise transects parallel to the western coasts of the continental U.S. and Canada. For each of these components, measurements were collected in multiple seasons.

Here, results are reported from the project funded by U.S. Coast Guard (USCG). Additional data obtained from related projects in the eastern North Pacific that were funded by California State Lands Commission and National Sea Grant Program were also included. These data were combined to test whether differences in tracer concentrations could provide a robust method to discriminate water from ports versus oceanic water, examining the effect of season, geographic location, and distance from shore on results.

2 METHODS

2.1 Experimental and Sampling Design

Samples were collected from surface waters in selected estuaries with major ports, and along transects extending to various distances from shore, to measure concentrations of CDOM and trace elements at sites in the eastern and western Pacific. For transects, the sampling strategy included perpendicular offshore transects and coastwise (parallel to shore) transects. Offshore transects provide detailed longitudinal information on the rate of decline of terrestrial signals with distance from specific regions of the coast, usually ports. Coastwise transects run essentially North/South along the western coast of the United States, providing information on the latitudinal variability in tracer penetration from the coast.

In this report, data are included that were collected from three different agencies (USCG, National Sea Grant, and the California State Lands Commission), which combine to provide broad coverage. Together, analyses of the U.S. West Coast included intensive quarterly events for three port systems, four offshore transect locations, and within the Strait of Juan de Fuca (an approximately 80 nmi long passage connecting Puget Sound and the Strait of Georgia to the Pacific). Biannual (usually summer and winter) port sampling occurred for five targeted ports in Asia and Canada, with intermittent (usually biannual) offshore transects conducted at six other U.S. locations. Further coastwise surveys along the U.S West Coast and between Japan and Alaska were conducted opportunistically with the dual aim of maximizing latitudinal spread and repeating seasonal coverage where possible. For the West Coast or North America, sites were grouped into regional zones (A–E, Figure 1) and analyzed collectively, allowing tracer concentrations and variability to be examined along a latitudinal gradient.

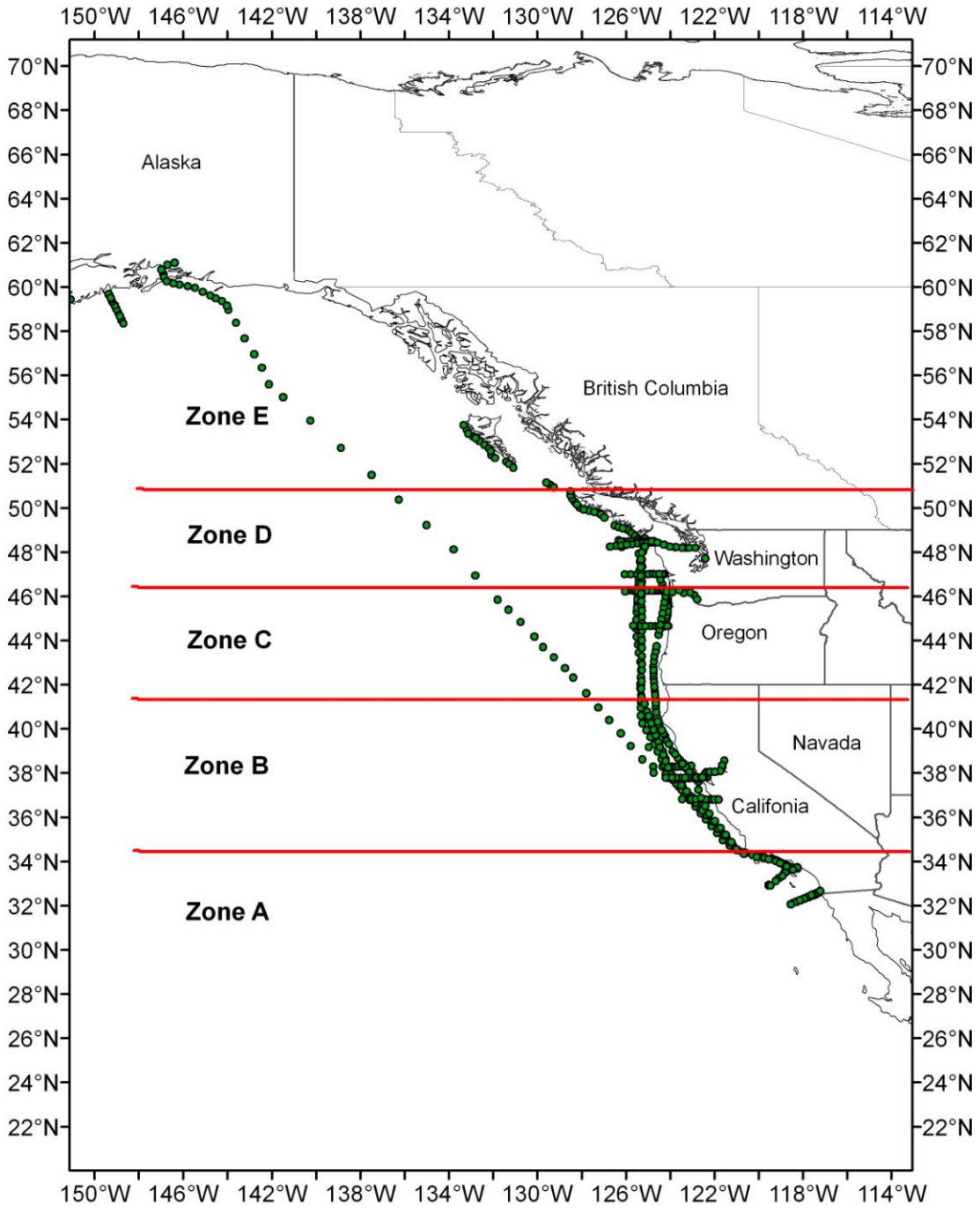

Figure 1. Sampling regions (zones A–E) and sites (circles) along the U.S. West Coast.

2.1.1 Port Surveys

Port systems were selected based on volume of shipping traffic and included a broad range of geographic sizes and locations. Previous studies, funded by National Seagrant and California State Lands Commission (Boehme et al., 2008; Murphy et al., 2007a), examined four major port systems in western North America: Los Angeles and Long Beach, San Francisco Bay, Puget Sound, and the Strait of Georgia.

In the current study, funded by USCG, international ports in Asia that deliver significant cargo volume to the U.S. were also examined, including: Hong Kong, China; Kaohsiung, Taiwan; Tokyo Bay, Japan; and the harbor and surrounding environment of Busan, South Korea. Collaborations were established with local researchers in all locations, allowing sample collection and data-sharing data with scientists in the host countries. The port surveys are summarized in Table 1.

Table 1. Summary of port surveys.

Event Code	Season	Port Location	Port area (km^2)	No. Sites	Dates	Funding source
SF-p-win	Winter	San Francisco Bay, CA	937	24	Feb 8–9 2006	NSG
SF-p-spr	Spring	San Francisco Bay, CA	937	12	Apr 6–7 2006	NSG
SF-p-sum	Summer	San Francisco Bay, CA	937	24	Jul 28–29 2006	NSG
SF-p-fall	Fall	San Francisco Bay, CA	937	12	Oct 27 2006	NSG
PS-p-sum	Summer	Puget Sound, WA	1650	24	Jun 20–23 2006	NSG
PS-p-fall	Fall	Puget Sound, WA	1650	12	Oct 3–6 2006	NSG
PS-p-win	Winter	Puget Sound, WA	1650	24	Jan 21–26 2007	NSG
PS-p-spr	Spring	Puget Sound, WA	1650	12	May 7–8 2007	NSG
SG-p-sum	Summer	Strait of Georgia, CAN	3708	21	Jul 5–7 2006	NSG
SG-p-win	Winter	Strait of Georgia, CAN	3708	24	Feb 1–9 2007	NSG
LA-p-win	Winter	Los Angeles / Long Beach, CA	51	24	Feb 8–9 2006	CSLC
LA-p-spr	Spring	Los Angeles / Long Beach, CA	51	12	Apr 6–7 2006	CSLC
LA-p-sum	Summer	Los Angeles / Long Beach, CA	51	24	Jul 28–29 2006	CSLC
LA-p-fall	Fall	Los Angeles / Long Beach, CA	51	12	Oct 27 2006	CSLC
TW-p-win	Winter	Kaohsiung, Taiwan	10	24	Mar 6–9 2007	USCG
TW-p-sum	Summer	Kaohsiung, Taiwan	10	24	Aug 17–20 2006	USCG
HK-p-win	Winter	Hong Kong, China	312	24	Feb 27–Mar 1 2007	USCG
HK-p-sum	Summer	Hong Kong, China	312	24	Aug 23–25 2006	USCG
JP-p-win	Winter	Tokyo Bay, Japan	1157	24	Mar 7–8 2007	USCG
JP-p-sum	Summer	Tokyo Bay, Japan	1157	23	Jun 25–26 2008	USCG
KR-p-win	Winter	Busan, Korea	351	24	Feb 27–28 2008	USCG
KR-p-sum	Summer	Busan, Korea	351	24	Aug 21–23 2007	USCG

The sampling design at each port was as follows. Each port was divided into a number of strata, usually 8, each of which was sub-sampled in a consistent manner. Within each stratum, three discrete sites were sampled, including a site near a prominent anthropogenic feature (e.g., a terminal, dock, etc.), a deep channel site (usually the navigation channel) and a shallow site near the margins (approximately 7–20 meters (m) deep). This range of sites was selected to encompass variation expected in estuaries, due to potential influences of various natural processes and human activities. Replicate samples were collected from 24 sites in summer and winter spatial surveys, to measure seasonal (temporal) variation corresponding roughly to the wet and dry seasons, yielding a total of approximately 580 samples across ports for analysis of CDOM and trace elements each (Table 2). For previous studies of the western U.S. port systems, additional samples were collected in identical fashion from a subset of sites (usually 12) for finer resolution of temporal variation (Boehme et al., 2008; Murphy et al., 2007a) .

Table 2. Foreign port survey sampling effort.

Event Code	Season	Port Location	N:CDOM	N: Trace elements	N: Water quality
TW-p-win	Winter	Kaohsiung, Taiwan	72	72	175
TW-p-sum	Summer	Kaohsiung, Taiwan	72	72	120
HK-p-win	Winter	Hong Kong, China	72	72	120
HK-p-sum	Summer	Hong Kong, China	72	72	121
JP-p-win	Winter	Tokyo Bay, Japan	69	70	115
JP-p-sum	Summer	Tokyo Bay, Japan	72	73	115
KR-p-win	Winter	Busan, Korea	75	75	121
KR-p-sum	Summer	Busan, Korea	75	75	121
Totals			**579**	**581**	**953**

At each site, three replicate tracer samples were obtained at approximately a 5-m depth for analysis of CDOM and trace elements. In addition, water quality parameters (salinity, temperature, conductivity, dissolved oxygen, and pH) were recorded at five depths.

2.1.2 Offshore Transects

Sampling along offshore transects was conducted predominantly from small research vessels and charter boats with locations selected to encompass multiple regions and major estuaries and river systems found along western North America. These offshore transects were oriented approximately perpendicular to shore west of: San Diego, Los Angeles, Bodega Bay, Monterey Bay, and San Francisco Bay (CA); Gray's Harbor and Newport (OR); the Columbia River and the Strait of Juan de Fuca west of Puget Sound (WA); and Seward (AK). At four of these locations, transects were repeated in multiple seasons to examine temporal variation. In total, sampling occurred on 24 offshore transects, when combining results from the current and previous studies (Table 3).

For offshore transects, sampling was conducted at 12 or 13 sites along each cruise track, with cruise tracks varying in length from 60 to 80 nmi. Plans for thirteen sampling sites per transect at fixed distances from the shore (80, 70, 60, 50, 40, 30, 20, 15, 10, 5, 2, 1, 0 nmi) were modified due to ship time constraints, with 70 nmi station occasionally omitted. Nearshore sampling sites were spaced more closely to maximize the information collected in coastal regions where greater concentration gradients were expected. Distance to shore was defined as the distance to the closest point on mainland excluding islands (except for mainland designation for Vancouver Island).

Table 3. Summary of West Coast offshore transects.

Event Code	Season	Region A-E	Geographic location	Transect length (nmi)	No. sites	Dates	Fund
SD-o-fall	Fall	A	San Diego, CA	76	13	Sep 13–14, 2006	CSLC
SD-o-sum	Summer	A	San Diego, CA	76	12	Jun 24, 2007	CSLC
LB-o-spr	Spring	A	Long Beach, CA	81	12	Apr 12–13, 2006	CSLC
LB-o-sum	Summer	A	Long Beach, CA	80	12	Jul 2–3, 2006	CSLC
LB-o-fall	Fall	A	Long Beach, CA	81	12	Nov 6–7, 2006	CSLC
LB-o-win	Winter	A	Long Beach, CA	77	12	Feb 20–21, 2007	CSLC
JDS-o-sum	Summer	D	Juan de Fuca Strait, WA	61	12	Jun 17–18, 2006	Seagrant
JDF-o-fall	Fall	D	Juan de Fuca Strait, WA	70	11	Sep 15–Oct 9, 2007	USCG
JDS-o-win	Winter	D	Juan de Fuca Strait, WA	80	13	Jan 16–18, 2007	Seagrant
JDS-o-spr	Spring	D	Juan de Fuca Strait, WA	80	12	May 14–15, 2007	USCG
SFB-o-win	Winter	B	San Francisco Bay, CA	67	11	Feb 24, 2007	Seagrant
SFB-o-spr	Spring	B	San Francisco Bay, CA	81	11	Apr 20, 2007	USCG
SFB-o-sum	Summer	B	San Francisco Bay, CA	68	12	Sep 5, 2006	Seagrant
SFB-o-fall	Fall	B	San Francisco Bay, CA	84	11	Oct 29–30, 2006	Seagrant
RB-o-spr	Spring	E	Resurrection Bay, AK	83	13	May 21–22, 2006	USCG
New-o-fall	Fall	D	Newport, OR	67	20	Sep 26–27, 2006; Oct 12–18, 2006	USCG
GH-o-fall	Fall	D	Grays Harbor, WA	75	13	Oct 12–18, 2007	USCG
CR-o-fall(1)	Fall	C	Columbia River (OR & WA)	75	13	Oct 12–18, 2008	USCG
CR-o-spr	Spring	C	Columbia River (OR & WA)	79	13	May 18–91, 2007	USCG
CR-o-fall(2)	Fall	C	Columbia River (OR & WA)	79	12	Nov 23–24, 2007	USCG
MB-o-fall	Fall	B	Monterey Bay, CA	80	12	Oct 15, 2007	USCG
BB-o-fall	Fall	B	Bodega Bay, CA	80	13	Oct 13, 2007	USCG
JP-t-spr	Spring	-	Transpacific from Chiba, JP to Nikiski, AK	-	61	Mar 10–18, 2007	USCG
JP-t-sum	Summer	-	Transpacific from Yokohama, JP to Nikiski, AK	-	63	Aug 30–Sep 8, 2007	USCG

Three replicate samples for each class of chemical tracer (CDOM and trace metals) were collected from a depth of 5 m at each site, and water quality parameters (salinity, temperature, conductivity, dissolved oxygen, and pH) were recorded at the same depth. Total number of samples collected for each cruise is shown in Table 4, with more than 1,000 samples collected for analysis of CDOM and trace elements.

Table 4. Pacific offshore transect sampling effort.

Event Code	Season	Geographic location	N: CDOM	N: Trace elements	N: Water quality
SD-o-fall	Fall	San Diego, CA	39	39	91
SD-o-sum	Summer	San Diego, CA	36	36	84
LB-o-spr	Spring	Long Beach, CA	36	36	84
LB-o-sum	Summer	Long Beach, CA	36	36	84
LB-o-fall	Fall	Long Beach, CA	36	36	276
LB-o-win	Winter	Long Beach, CA	36	36	84
JDS-o-sum	Summer	Juan de Fuca Strait, WA	24	24	126
JDF-c-fall	Fall	Juan de Fuca Strait, WA	36	36	361
JDS-o-win	Winter	Juan de Fuca Strait, WA	66	66	151
JDS-o-spr	Spring	Juan de Fuca Strait, WA	63	63	126
SFB-o-win	Winter	San Francisco Bay, CA	33	33	55
SFB-o-spr	Spring	San Francisco Bay, CA	33	33	220
SFB-o-sum	Summer	San Francisco Bay, CA	36	36	56
SFB-o-fall	Fall	San Francisco Bay, CA	33	33	237
RB-o-spr	Spring	Resurrection Bay, AK	36	36	72
New-o-fall	Fall	Newport, OR	49	49	63
GH-o-fall	Fall	Grays Harbor, WA	28	28	91
CR-o-fall(1)	Fall	Columbia River (OR & WA)	28	28	98
CR-o-spr	Spring	Columbia River (OR & WA)	36	36	242
CR-o-fall(2)	Fall	Columbia River (OR & WA)	36	37	326
MB-o-fall	Fall	Monterey Bay, CA	36	36	290
BB-o-fall	Fall	Bodega Bay, CA	36	36	285
JP-t-spr	Spring	Transpacific from Chiba, JP to Nikiski, AK	184	152	422
JP-t-sum	Summer	Transpacific from Yokohama, JP to Nikiski, AK	189	135	438
Totals			**1201**	**1116**	**4362**

2.1.3 Coastwise Transects

Sampling was conducted along eight coastwise transects for various portions of North America, from southern California to Alaska. All sampling for coastwise transects was done on commercial vessels, selected to include multiple regions and seasons (Table 5).

Table 5. Summary of West Coast coastwise transects.

Event Code	Season	Region A-E	Description	Transect length (nmi)	No. sites	Dates	Fund
Oak-c-sum	Summer	A-B	Oakland to Long Beach	400	26	Aug 17–18, 2006	CSLC
Sac-c-fall	Fall	B-D	Sacramento to Vancouver, WA	697	59	Nov 26–28, 2005	CSLC
LA-c-spr	Spring	A-D	Los Angeles to Port Townsend	1112	60	Apr 22–25, 2007	USCG
LA-c-sum	Summer	A-D	Los Angeles to Port Townsend	1112	58	Aug 27–30, 2007	USCG
New-c-fall	Fall	C-D	Newport to Grays Harbor	134	14	Oct 12–18, 2006	USCG
Ben-c-fall	Fall	B-E	Benicia, CA to Vadlez, AK	1804	48	Oct 5–19, 2008	USCG
LA-c-win	Winter	A-D	Los Angeles to Port Townsend	1132	62	Dec 7–11, 2006	USCG
JDF-c-spr	Spring	D-E	JDF to AK border	477	44	May 12–Jun 9, 2007	USCG

Vessel routes followed the coasts of CA, OR, WA and AK, and were generally within 20nmi of shore for much of the voyages. Samples stations were spaced at approximately 3 to 10 nmi apart when vessels were outbound and inbound from port, and up to 100 nmi apart elsewhere in the ship's track. For all coastwise transects combined, 1,038 samples were collected for analysis of CDOM, and another 876 samples were collected for analysis of trace elements (Table 6).

Table 6. West Coast coastwise transect sampling effort.

Event Code			N: CDOM	N: Trace Elements	N: Water quality
Oak-c-sum	Summer	Oakland to Long Beach	78	78	182
Sac-c-fall	Fall	Sacramento to Vancouver, WA	96	96	236
LA-c-spr	Spring	Los Angeles to Port Townsend	183	183	366
LA-c-sum	Summer	Los Angeles to Port Townsend	180	180	351
New-c-fall	Fall	Newport to Grays Harbor	28	28	112
Ben-c-fall	Fall	Benicia, CA to Vadlez, AK	144	105	313
LA-c-win	Winter	Los Angeles to Port Townsend	186	186	372
JDF-c-spr	Spring	JDF to AK border	143	20	268
Totals			**1038**	**876**	**2200**

2.2 Sample Collection

2.2.1 Preparation of Sampling Equipment

Tubing (Teflon and Masterflex) was soaked in an acid bath of 4 normal (N) hydrochloric acid (HCl) for one week, then rinsed in laboratory grade water and sealed for shipping. Inline filters were soaked in 4 N HCl for one week, rinsed with laboratory grade water, then soaked in 4 N nitric acid (HNO_3) for another week, and rinsed again before being sealed for shipping. CDOM samples were collected in amber glass bottles that were detergent-washed then baked at 450 degrees Celsius (°C) for at least eight hours. Centrifuge tubes for trace element samples were purchased pre-prepared from SPI Supplies (West Chester, PA). Equipment was cleaned in the laboratory between events, and contamination was minimized by flushing sampling apparatus with at least 5 liters (L) of water (more than 10 times internal tubing and filter volume) prior to sampling.

2.2.2 Seawater Access

During port surveys and offshore transects, seawater was generally accessed over the side of small chartered boats and research vessels. In these cases, samples were collected using a peristaltic pump (Cole Parmer 7533-60 12vDC) fitted with rigid Teflon tubing (1/4-inch inside diameter x 7 meters (m) with a 500-gram (g) weight on outboard end) and flexible Masterflex (1 m) tubing and connected to an inline 0.45 micron (µm) capsule filter (GE Memtrex MP). In general, samples were collected for tracer analyses at 5-m depth and associated water quality data were measured from 1, 2, 3, 5, and 10 m depth. Samples were collected at shallower depths only when 1) the maximum water depth at the site was less than 5 m, or 2) strong wind-drift and/or currents displaced the tubing from its intended vertical orientation. For example, the mouth of a 5-m hose angled at 45 degrees from vertical is positioned at ~ 3.5-m depth.

Sample collection aboard the research vessel (R/V) Thomas G. Thompson was conducted underway via purpose-built clean seawater sampling pipes circulating flowing sea-water in the onboard lab. Flow from the seawater system nozzle could be manually adjusted, and a direct connection to a capsule filter via Masterflex tubing circumvented the need for a pump.

Coastwise transect samples were also collected underway aboard commercial vessels via the ship's engine cooling system, which constantly circulates ambient seawater from 4–9-m depth through steel pipes at flow rates of ~ 200 cubic meters (m^3) per hour. Samples were collected using a filter and tubing assembly attached to the pipe as near as possible to the seawater intake and upstream of engine machinery.

2.2.3 CDOM and Trace Element Sampling

Trace element and CDOM samples were collected according to published protocols (Murphy et al., 2004b). Samples were frozen then sent to specialist analytical laboratories for analysis. CDOM samples were analyzed at the Smithsonian Environmental Research Center, Maryland and trace element samples at Rutgers University, New Jersey.

2.2.4 Water Quality Measurements

Salinity, temperature, and conductivity were measured using in-situ handheld probes (YSI-85, YSI Inc.). As part of dual-measurement salinity quality assurance practices, the Environmental Protection Agency has routinely compared handheld refractometers with Hydrolab DataSonde 3/ Surveyor 4 units (used for in-situ monitoring purposes by the National Coastal Assessment program) and has listed acceptable usage tolerances of ± 3 psu between the two methods (Strobel and Heitmuller, 2001). In this study, intercalibration exercises in May and October 2007 with a YSI-556 indicated some offsets had occurred when calibrating the YSI-85 units, or that some units did not maintain their calibrations over time. For measurements in this study, salinity data are considered accurate to ± 2 practical salinity units (psu) (± 8 percent), which is comparable to the accuracy of measurements for CDOM and trace elements. Corrected salinity data and maps of its regional distribution are available in the appendices.

Water pH was measured using a handheld probe (Waterproof pH Tester BNC, Oakton Instruments). The pH probe was calibrated against standards (4.01, 7.00, and 10.01) at the beginning of every sampling day.

2.2.5 Global Positioning System Locations and Distance to Shore

Sampling positions were recorded using hand-held GPS units (Garmin GPSMAP 76CSx). Coordinates were recorded upon arrival to and departure from sites to account for possible drift during the approximately 15-minute sampling interval. Coordinates are considered accurate to less than 50 m while the boat drifted during offshore transects and port surveys. Distance from shore was calculated for all offshore transect sites via navigational chart measurements or MATLAB calculations performed with the seawater toolbox of the Commonwealth Scientific and Industrial Research Organization, Australia (CSIRO, Version 1.4), utilizing coastal boundaries obtained from the coastline extractor website of the National Oceanographic and Atmospheric Administration (NOAA) and represent mean location at mean tide (http://www.ngdc.noaa.gov/mgg/shorelines/shorelines.html).

2.3 Sample Analysis

All sample replicates were analyzed for port surveys. For coastwise and offshore sampling events, the general procedure was to analyze two of three replicates collected from each site, reserving an additional replicate in cold storage. This reduced analysis costs while allowing for the replacement of broken samples or the examination of additional replicates if contradictory results were obtained from the two primary replicates.

2.3.1 Trace Elements

2.3.1.1 Analytical Measurements

The concentrations of Ba, Mn, molybdenum (Mo) and P were analyzed on an Element-1 high resolution inductively coupled plasma mass spectrometer (ThermoFinnigan, Bremen, Germany) at Rutgers Inorganic Analytical Laboratory, Institute of Marine and Coastal Sciences, Rutgers the State University of New Jersey. Samples were diluted ten-fold with 10 percent volume-to-volume ultra-pure HNO_3 then analyzed in low and medium resolution using published techniques (Field et al., 2007).

With the exception of coastwise transects, concentrations presented are means of replicate samples (N = 2-3) subject to the removal of outlier data detected according to methods described below.

2.3.1.2 Outlier Detection

Diagnostic tests were performed to identify outliers due to sample contamination or analytical error, providing standardized criteria for evaluating data quality and when to exclude specific observations from further analyses. Quality assurance/quality control (QA/QC) were performed individually for Ba, P, and Mn. Values presented are means (N = 1-3) of data retained after QA/QC procedures were implemented as described in this section. Individual site data for trace elements can be found in the appendices.

First, percent differences among replicate measurements were calculated and compared to published accuracy and precision standards for individual tracers (Field et al., 2007). If the range of replicate measurements was greater than twice the expected precision for a given tracer (Table 3 in Field et al., 2007), the samples were flagged as potentially encompassing erroneous data and subject to further scrutiny.

Where samples were analyzed in triplicate, outlier measurements for Ba, P, and Mn were identified using Dixon's Q-test at a 95 percent confidence level. Data that failed the statistical test were substituted with missing values, and where two or more tracers in a sample failed the Q-test, all data for the affected sample were deleted.

Where samples were analyzed in duplicate, the occurrence of high inter-replicate variability suggested that at least one of the samples was probably an outlier. In the case that a third replicate sample had been collected (but not analyzed), the third replicate was sent to Rutgers for analysis and QA/QC performed on the triplicate measurements as described above. In the case that no additional samples existed, both suspect samples were reanalyzed. If data were significantly different following reanalysis and meeting the criteria outlined above, the original data were replaced, otherwise, the data were averaged. There is no reliable way to diagnose outliers in unreplicated samples; therefore, all unreplicated measurements were retained in the dataset.

2.3.2 Chromophoric Dissolved Organic Matter (CDOM)

2.3.2.1 Fluorescence Measurements

Fluorescence matrices of CDOM were generated at SERC with a SPEX Fluorolog-3 from Horiba Jobin Yvon (Edison, New Jersey, U.S.A). Undiluted filtered seawater samples were analyzed in ratio mode using a 0.5 second integration time and a 1-centimeter (cm) quartz cell held at 20°C. Experimental bandpass was set to 5 nm for excitation and emission monochromators. The Fluorolog-3 is configured with a single excitation monochromator (1200 grooves/millimeter (mm)) blazed at 330 nm and a dual emission

monochromator (1200 grooves/mm) blazed at 500 nm, a water-cooled, red sensitive photomultiplier tube and a 450-watt Xenon arc lamp.

This technique produces a 3-dimensional characterization of each sample across all experimental wavelengths, referred to in this document as sample excitation emission matrices (EEMs). Sample EEMs were concatenated from individual emission (λ_{em}) scans from 300–600 nm collected every 4 nm, across an excitation range (λ_{ex}) of 235–455 nm every 5 nm. EEMs were corrected for instrumental and lamp variability and normalized to quinine sulfate fluorescence intensity as previously described (Coble et al., 1993; Mobed et al., 1996) using an in-house MATLAB program (Mathworks Inc., Version 7). Fluorescence intensity is expressed in units of parts per billion (ppb) quinine sulfate equivalents (QSE).

A second type of data identifies CDOM variability based on point measurements at specific wavelength pairs of interest, referred to here as CDOM tracers. CDOM tracers estimate CDOM concentrations reported via fluorescence intensities for five excitation/emission wavelength pairs as listed in the appendices.

The most robust estimates of CDOM concentration by fluorescence intensity occur when there is a linear relationship between concentration and intensity, which generally occurs when environmental CDOM concentrations are relatively low (Lackowicz, 1999). This relationship may become nonlinear at high CDOM concentrations due to inner filter effects (IFE). IFE arise in part from competition for excitation light by absorbing but non-fluorescent compounds that decrease the excitation radiance available to fluorophore in solution. IFE also occur when light emitted by sample fluorophores is reabsorbed by components in the sample, reducing the detected intensity of fluorescence. Both effects are more prevalent in concentrated CDOM solutions due to close proximity between the optically active components. High concentrations of CDOM are encountered in port, coastal and nearshore environments, and underestimation of CDOM levels in coastal and port waters due to IFE may result.

Operational limits for the onset of IFE in seawater samples have been defined using UV-VIS absorption of CDOM, based on absorbance (A) at two wavelengths: $A_{300} < 0.02$ in a 1-cm cell (Green and Blough, 1994) or $A_{350} < 0.02$ in a 1-cm cell (Moran et al., 2000). Boehme (J. Boehme, unpublished data) previously examined IFE in the Tampa Bay estuary, and found the fluorescence intensity related to the onset of inner filter effects fell between 16–20 QSE, which roughly corresponded to $A_{300} < 0.02$.

In this study, optically dilute samples were distinguished when the observed concentration of CDOM for the wavelength pair (λ_{ex} /λ_{em}) 350/450 nm fell below 10 QSE. IFE were considered negligible for optically dilute samples in this study. This was the case for more than 94.6 percent of the fluorescence samples presented here from this and companion studies in the region. The remaining concentrated samples were uniformly associated with port systems in Asia, the U.S and Canada, and coastal areas with depressed salinity (< 30 psu) near the Columbia River, Vancouver, WA and San Francisco, CA. For these sites, fluorescence intensities may be underestimated by up to 10 percent.

2.3.2.2 Outlier Detection

Diagnostic tests were performed to identify outliers due to contamination or analytical error, using a standardized approach to remove these data from the dataset. Values presented in this study are means (N = 1-3) of data retained after QA/QC procedures were implemented as described in this section. QA/QC was performed both upon sample EEMs and CDOM tracers at target wavelength pairs.

Sample outliers for EEMs were identified when (1) the fluorescence peaks were altered either by shape or number of peaks relative to its duplicate, and/or (2) the wavelength positions of major CDOM peaks differed between replicates. As with the trace elements, all unreplicated CDOM samples were retained in the dataset.

For duplicate samples, outlier CDOM tracers were flagged if fluorescence intensity was abnormally high relative to its duplicate. If additional replicate samples existed in frozen storage, these were analyzed for comparison to the outlier and added to the data set. For samples collected in triplicate, outlier CDOM tracers were identified using Dixon's Q-test (Rorabacher, 1991) on tracer fluorescence intensity.

3 RESULTS

Trace element and CDOM fluorescence data collected during surveys in the western and eastern Pacific facilitate examination of regional and seasonal trends and the relationship between tracer concentrations and distance from land. Ba, P, and Mn concentrations have demonstrated utility for tracing ballast water sources and are presented in detail in this report. Mo typically behaves conservatively with salinity; therefore limited data are included for comparison in Appendix A.

For CDOM, comparisons with previous studies are aided by the inclusion of horizontal threshold lines on figures. These thresholds for CDOM tracers C2* and C3* of 1.7 and 0.7 QSE, respectively, were considered by Murphy et al. (2006) to be optimal cutoff concentrations between unexchanged ballast water (high-CDOM) and exchanged ballast water (low-CDOM). Since all oceanic regions are potential source waters for ballast tanks, inclusion of threshold lines on plots facilitates the visual assessment of their wider applicability. However, it should be recognized that these thresholds were developed from a limited dataset of primarily ballast samples, which typically have elevated tracer levels relative to their ocean source (Murphy et al., 2008; Murphy et al., 2006). Thus, threshold lines on figures should be interpreted as upper limits for open ocean concentrations which, assuming 100 percent effective BWE, would correspond to concentrations measured in exchanged ballast tanks.

3.1 Spatial Influences on Tracer Distribution

3.1.1 Eastern Pacific: the U.S. West Coast

Figure 2 through Figure 6 show summary statistics for the distribution of chemical tracer concentrations in the eastern Pacific, in coastal and offshore environments commonly transited by commercial shipping routes. To display the north-south variability in tracer concentrations, results are displayed by each of the five regional zones (see Section 2.1). Detailed maps for observed tracer concentrations are provided in Appendices A–F.

Trace elements typically displayed elevated concentrations in and near ports, but variable trends with increasing distance from land were observed. On the U.S. West Coast, Ba, Mn and P concentrations were highest in northern latitudes and tended to decrease in a southerly direction at a fixed distance from the coast. Thus tracer concentrations were lowest in Region A, corresponding to the southernmost latitudes in the study in the vicinity of San Diego and Los Angeles, CA. The low concentrations of all three trace elements in Region A reflect the much lower delivery of freshwater to this system compared to the northern latitudes.

Trace element concentrations in U.S. ports exhibited wide ranges, particularly for P and Mn. Ba, which ranged over an order of magnitude between 4–60 μgL^{-1} in port (Figure 2, top panel). In comparison, P ranged over 2 orders of magnitude between 10–200 μgL^{-1} (Figure 3, top panel) and Mn between 0.4–40 μgL^{-1} in ports (Figure 4, top panel). Average P concentrations less than 0.2 nmi from shore were highest off northern California (40–100 μgL^{-1}), and lowest (10–40 μgL^{-1}) off southern California (Region A). Ba (19–30 μgL^{-1}) and Mn (8–25 μgL^{-1}) were similarly elevated near northern California.

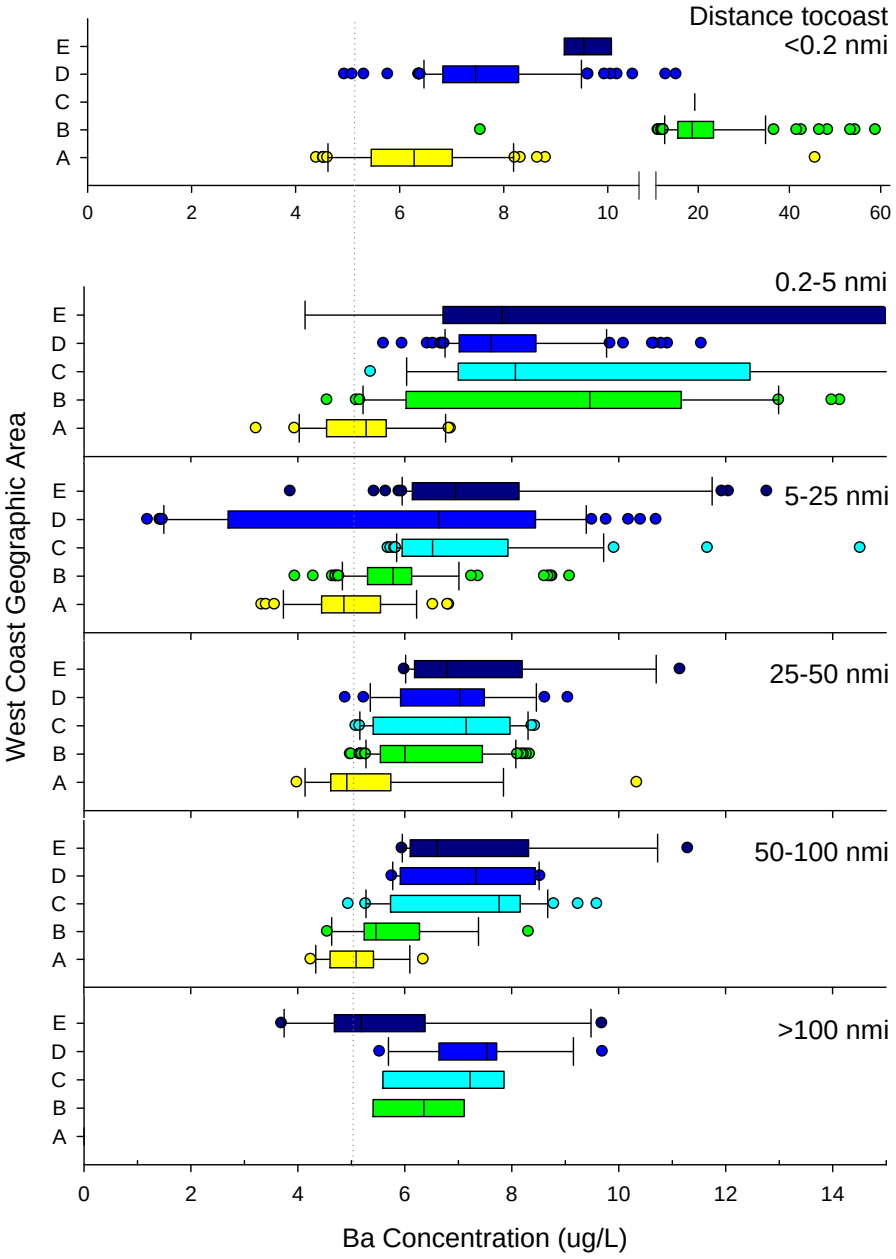

Figure 2. Barium distributions pooled by region (A–E) and distance from shore categories on the U.S. West Coast. Refer to Figure 1 for map of U.S. West Coast regions. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

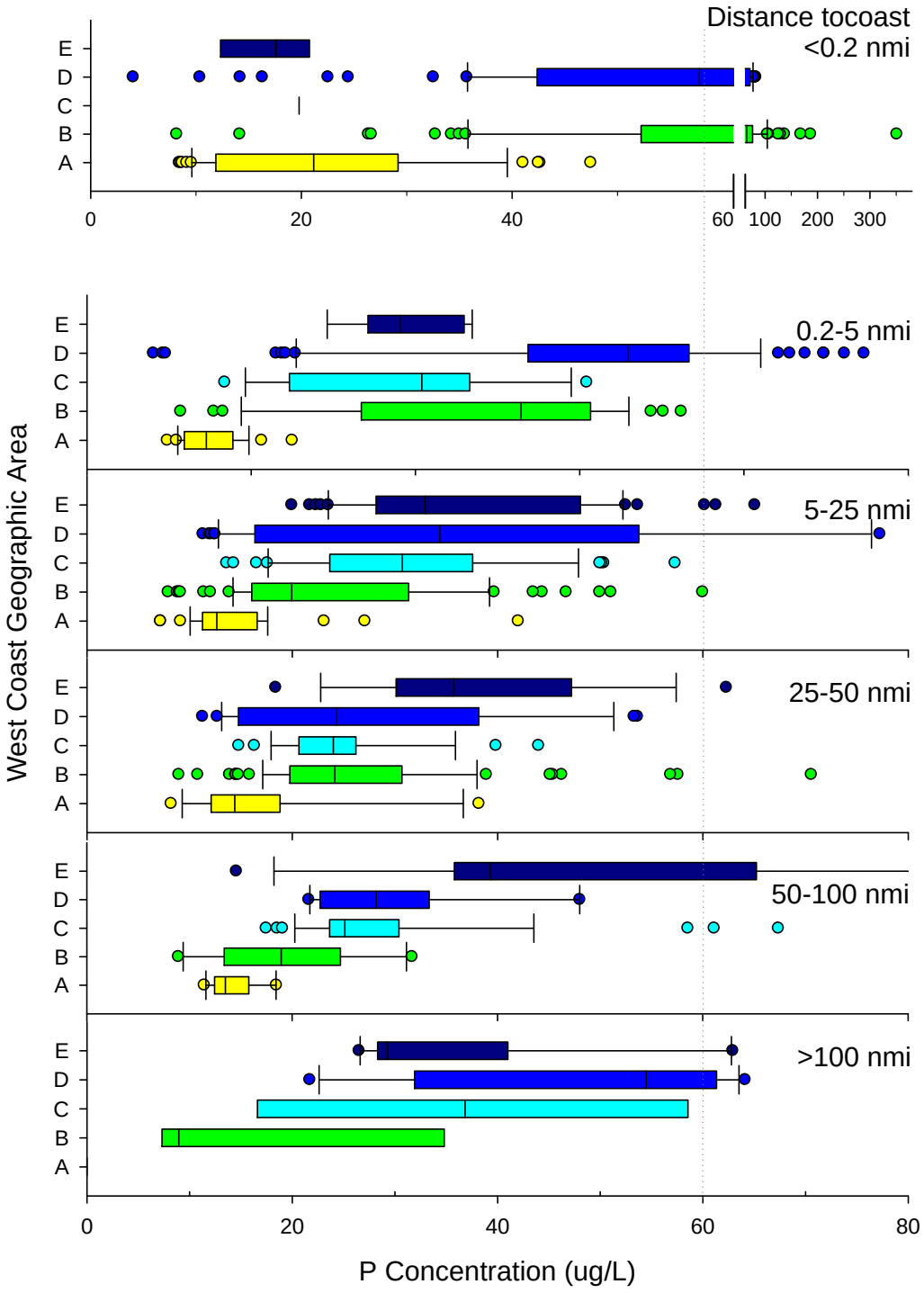

Figure 3. Phosphorus distributions pooled by region (A–E) and distance from shore categories on the U.S. West Coast. Refer to Figure 1 for map of U.S. West Coast regions. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

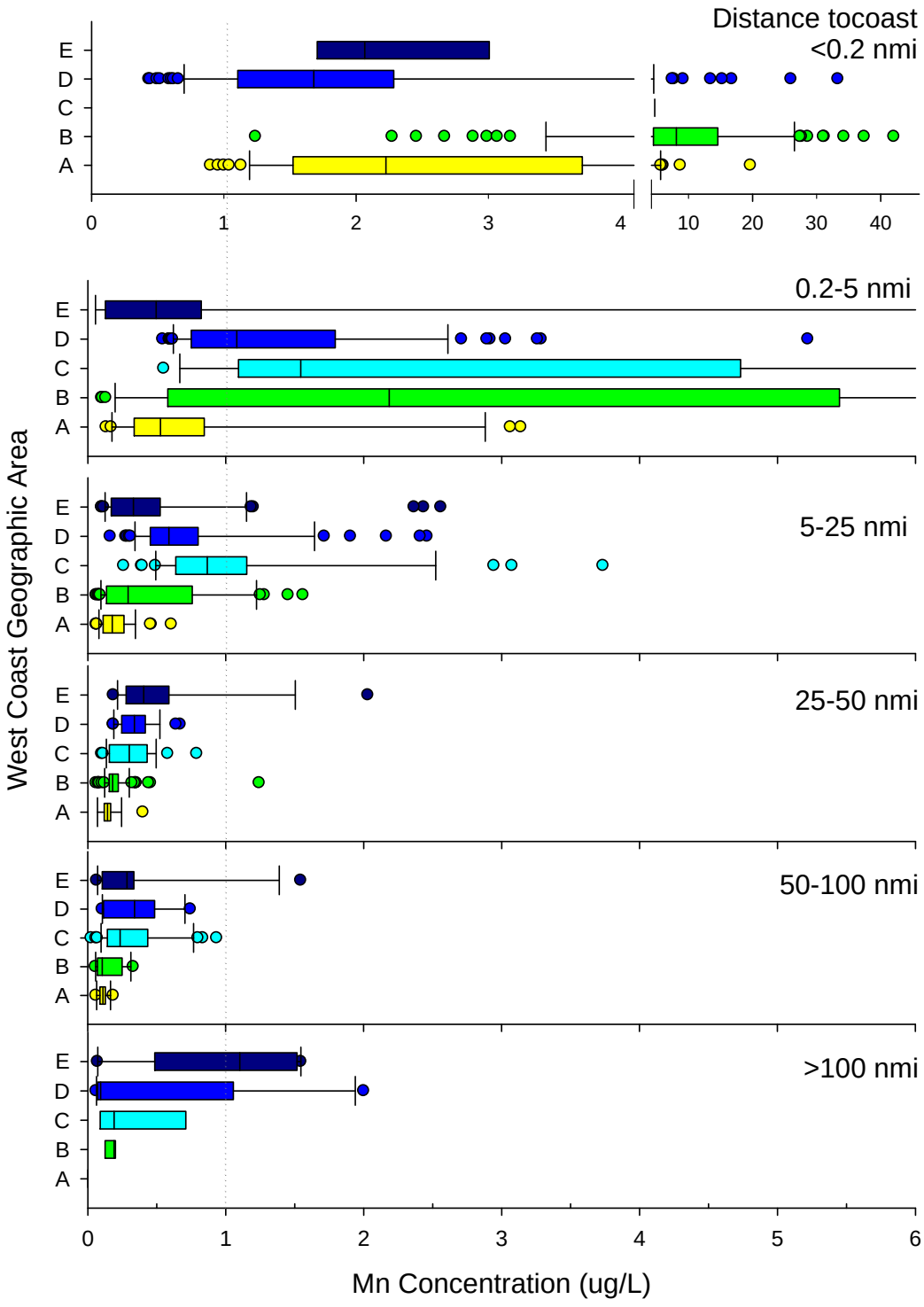

Figure 4. Manganese distributions pooled by region (A–E) and distance from shore categories on the U.S. West Coast. Refer to Figure 1 for map of U.S. West Coast regions. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

Strong regional differences in offshore decay profiles were apparent for Ba and P. Concentrations of both tracers typically decreased within 5 nmi of land in Regions A, B and D, then rebounded between 2–25 nmi from shore for both tracers in all regions, in some cases surpassing nearshore (<0.2 nmi) concentrations in northern latitudes (Regions C–E). Further decreases were observed between 25–100 nmi, where the lowest levels of Ba (4 to 11 μgL^{-1}) were observed despite P variability remaining high (15 to 100 μgL^{-1}). In contrast, Mn concentrations followed a more classical exponential decline, resulting in offshore baseline concentrations of approximately 0.12–0.5 μgL^{-1} that were achieved within 10–50 nmi of the coast.

Across the entire study, Ba and P concentrations at offshore (> 50 nmi) sites were much more variable than were Mn concentrations. In offshore sites, mean tracer concentrations in the eastern north Pacific were between 4 to 8 μgL^{-1} for Ba, 11 to 50 μgL^{-1} for P, and 0 to 1 μgL^{-1} for Mn.

Figure 5 and Figure 6 show trends in CDOM (C2* and C3*) in the eastern Pacific for each of the five regional zones. The positioning of a site along a north-south gradient had a major influence upon concentrations measured in the ocean along the U.S. West Coast. As seen in previous studies (Murphy et al., 2008), fluorescence intensities of C2* and C3* were highly correlated and displayed similar trends.

In and near West Coast ports (Figure 5 and Figure 6, top panel), C2* and C3* ranged over an order of magnitude between approximately 1.5–25 ppb QSE (C2*) and 0.6–19 QSE (C3*). The highest near shore CDOM concentrations occurred in northern California (Region B) and coastal Oregon (Region C), where they typically ranged from 10 to 20 ppb QSE for C2* and 5 to 12 QSE for C3*. Lower CDOM concentrations occurred in southern California (Region A), coastal Canada and Alaska (Region E) where concentrations ranged from 1 to 1.5 QSE for C2* 0.5 to 1 QSE for C3*.

In the ocean, C2* and C3* intensities decreased consistently with distance from land in all five West Coast regions. Thus, in Regions A–D, CDOM levels decreased by approximately 30 percent within 5 nmi of the mainland (Figure 5 and Figure 6). In Region E, CDOM concentrations remained relatively stable until 5 nmi. Beyond 5 nmi offshore during each survey, CDOM levels gradually declined, reaching local oceanic concentrations (0.4 to 1.1 QSE at C2*) within 25–50 nmi of the mainland (Regions A, B, C) or 50 to 100 nmi (Regions D and E).

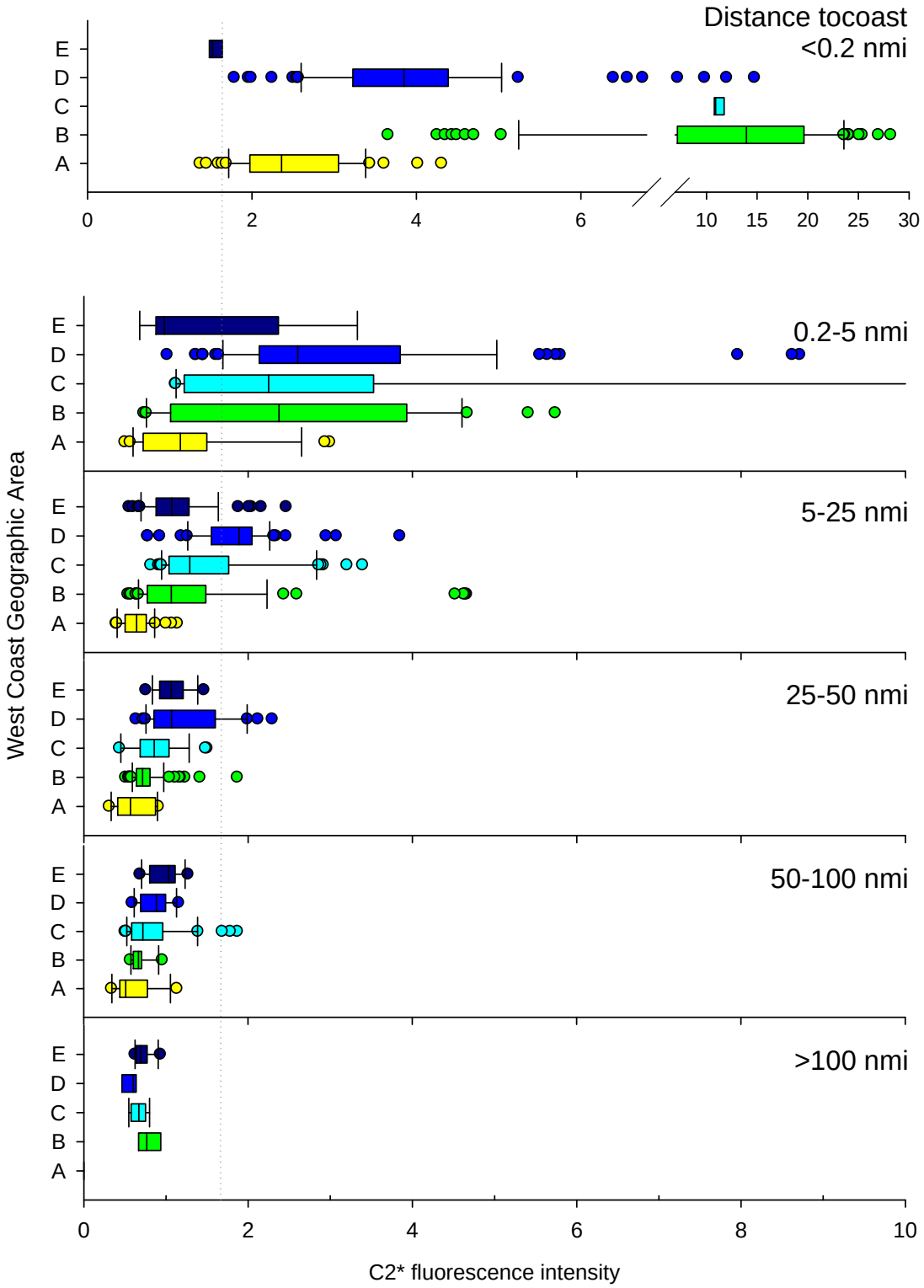

Figure 5. C2* distributions pooled by region (A–E) and distance from shore categories on the U.S. West Coast. Refer to Figure 1 for map of U.S. West Coast regions. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

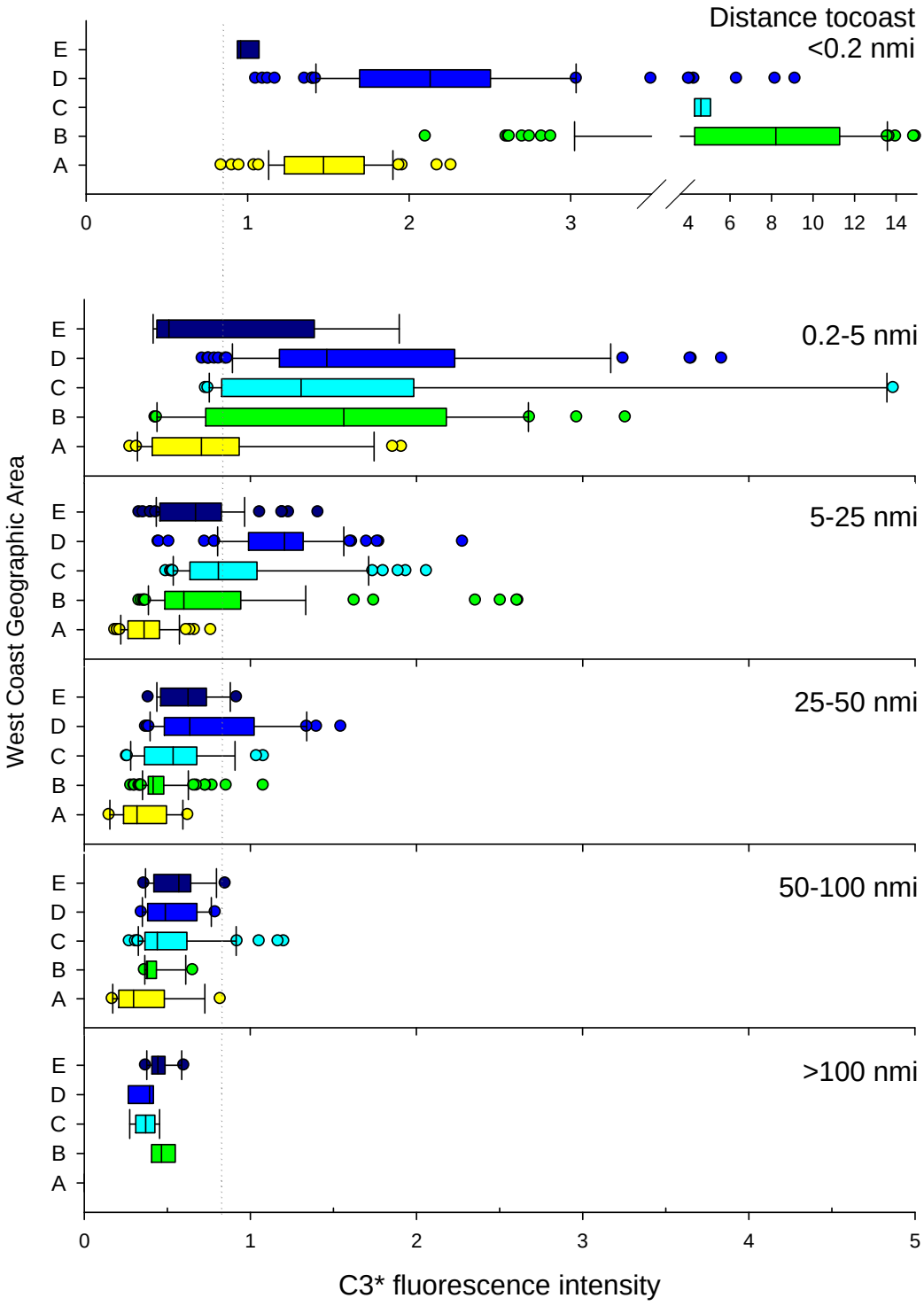

Figure 6. C3* distributions pooled by region (A–E) and distance from shore categories on the U.S. West Coast. Refer to Figure 1 for map of U.S. West Coast regions. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

3.1.2 Western Pacific: Asian Ports

The distributions of Ba, P and Mn during the biannual surveys in Tokyo Bay, Busan, Hong Kong and Kaohsiung are shown in (Figure 7). Overall, the distributions of the three trace elements were quite similar between Hong Kong and Busan, and between Tokyo Bay and Kaohsiung. Barium concentrations ranged between 6–8 μgL^{-1} in winter and 9–14 μgL^{-1} in summer. Phosphorus concentrations ranged more widely, with most samples within the range of 5–70 μgL^{-1}. Mn concentrations typically varied by an order of magnitude, from below 1 μgL^{-1} in Hong Kong and Tokyo Bay, to above 6 ugL^{-1} at one or more sites within each port. Only Mn concentrations were significantly higher in the Asian ports compared to the open ocean (Murphy et al., 2008, Appendix N).

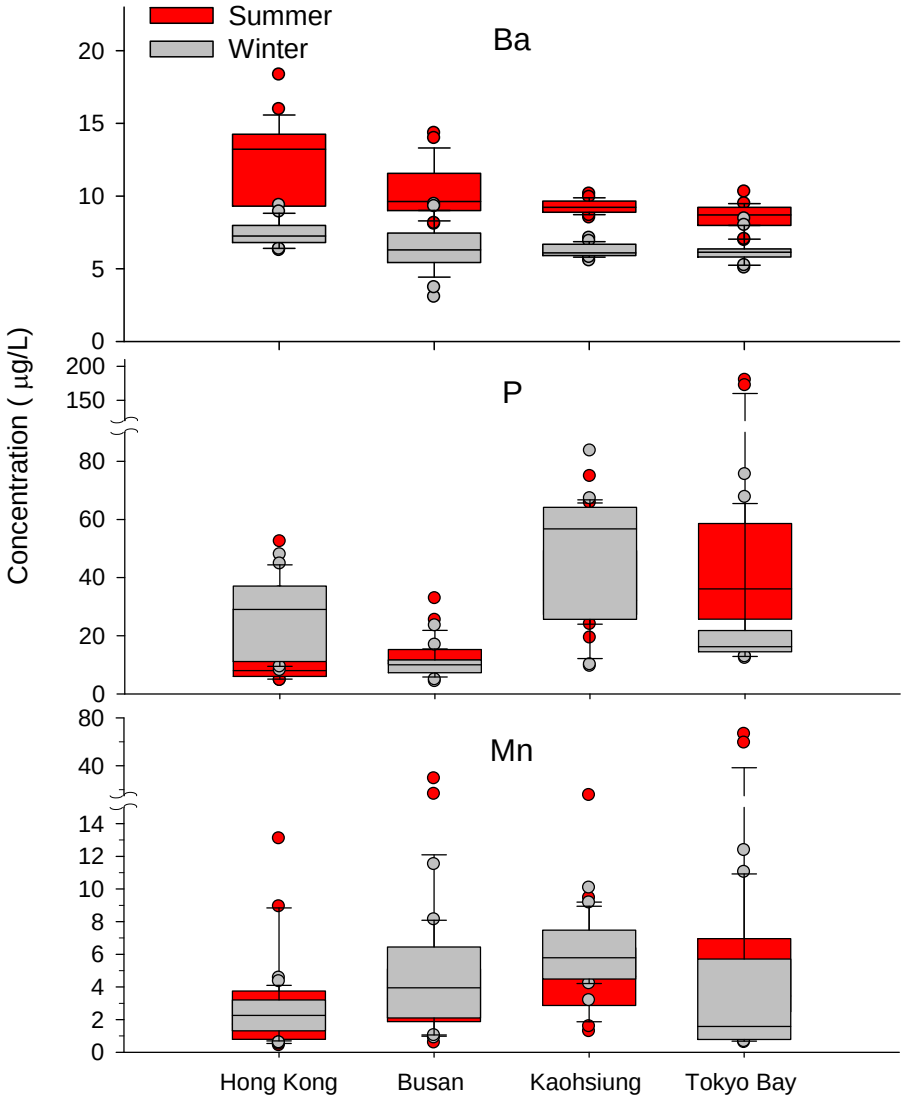

Figure 7. Barium (Ba), phosphorus (P) and manganese (Mn) in Asian ports during summer (orange) and winter (gray) surveys. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

Mean CDOM concentrations were higher in the four Asian ports than in the open ocean (>100 nmi) for all surveys (Coble, 1996; Murphy et al., 2004a; Murphy et al., 2007b). The seasonal distribution of CDOM in the Asian ports is illustrated for C2* and C3* in Figure 8. C2* concentrations exceeded C3* concentrations by a factor of approximately 1.7 at all sites sampled. C2* concentrations exhibited their lowest range of 0.51 to 5.8 QSE in Busan and their highest range of 0.86 to 10.4 QSE in Tokyo Bay. These trends were mimicked by C3* levels, with concentrations from 0.51 to 3.4 QSE in Busan and 0.57 to 6.1 QSE in Tokyo Bay. No systematic relationship was observed between CDOM concentration and the water depth at the sampling site or its proximity to human-made features.

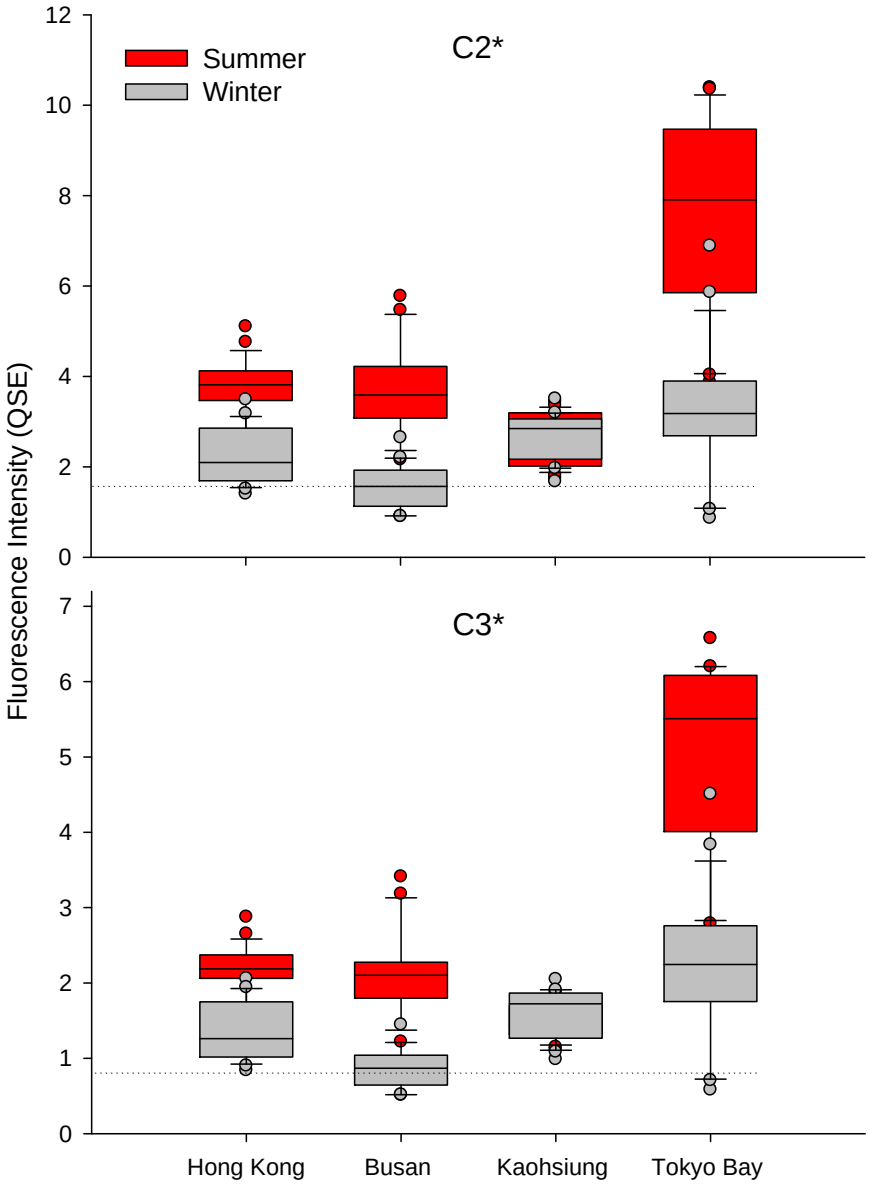

Figure 8. CDOM fluorescence intensities in Asian ports during summer (orange) and winter (gray) surveys. Boxes range from the lower 25% to upper 75% quartiles and are bisected by the median of the data. Whiskers extend to the highest and lowest data points, not including outliers indicated by circles.

3.2 Seasonal Influences on Tracer Distribution

3.2.1 Eastern Pacific: the U.S. West Coast

The relationship between tracer concentration and distance from the U.S. West Coast was seasonally as well as geographically variable (Figure 9). For Ba, mean concentrations at specific distances from land differed up to 2-fold between surveys conducted at different times of the year, with no noticeable contraction in this range observed at greater distances from shore. In comparison, P and Mn showed much smaller seasonal differences in average concentrations at distances of 25–100 nmi than within port or at distances exceeding 100 nmi.

Seasonal differences in offshore decay profiles were apparent for all trace elements. Typically, concentrations of Ba, Mn, and P decreased in first 25–50 nmi from the coast (Figure 2 through Figure 4) before stabilizing around 50 to 100 nmi from mainland. However, Ba and P concentrations reached different seasonal baselines at varying distances offshore. During the winter transect, Ba concentrations exceeding 20 μgL^{-1} in nearshore (<0.2 nmi) sites of Region B decreased to oceanic levels of approximately 6 μgL^{-1} within 10 nmi of the coast (Figure 9). In comparison during the summer transect, Ba decreased from around18 μgL^{-1} in the Bay to approximately 4.6 μgL^{-1} within 10 nmi of land. P in Region C increased in the fall from nearshore concentrations of approximately 20 μgL^{-1} to concentrations of 30 - 40 μgL^{-1} at around 5 nmi from shore (Figure 3 and Figure 9), then decreased again moving farther offshore. However, in winter, P concentrations were approximately stable near 70 μgL^{-1} at distances up to 5 nmi offshore.

In contrast to trace elements, CDOM distributions showed less seasonally variable trends with distance from shore in each region (Figure 10). CDOM concentrations ranged widely in port; however, samples collected from the same region tend to cluster together, indicating that differences between seasons were less important than differences between regions. In Region A (southern California), average fluorescence intensities varied little between seasons, although slightly elevated fluorescence intensities were recorded during the spring transect. In northern California (Region B), fluorescence was elevated in spring and winter nearshore (< 5 nmi) but was similar between seasons farther offshore. Seasonal sampling in Region C was limited, and no clear trends were apparent. In Region D, nearshore (< 5 nmi) CDOM fluorescence was highest in summer and lowest in fall, while offshore, mean fluorescence was highest in summer and fall and lowest in winter. Port sampling in Region E was limited to fall. During the offshore transects, fluorescence was lower in the spring than the fall and summer surveys.

Overall, the greatest seasonal variability was observed within 5 nmi from shore, with up to 2.5-fold differences in fluorescence magnitude between seasons observed in some regions. Farther offshore, seasonal differences were typically less than 2 fold. Also, since the seasonally averaged magnitude of CDOM fluorescence decreased typically 5 fold between port and the open ocean, the absolute magnitude of seasonal variation was much less in the ocean. Thus, at distances exceeding 50 nmi from the coast, seasonal differences in mean fluorescence intensity were always less than 0.5 ppb QSE.

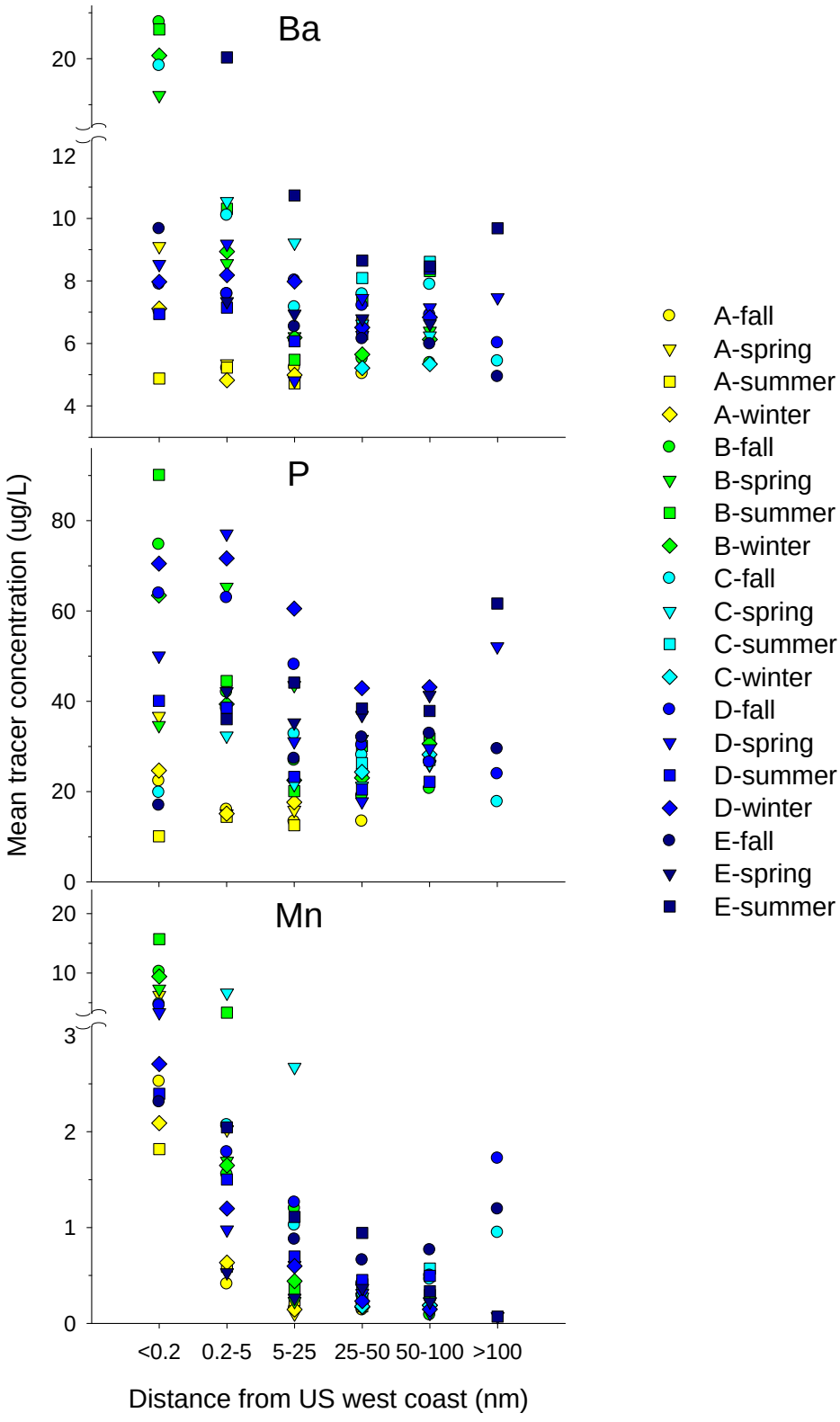

Figure 9. Seasonal changes in mean Ba, P and Mn concentrations, by zone (A–E) and distance from the U.S. West Coast. Refer to Figure 1 for map of regional zones.

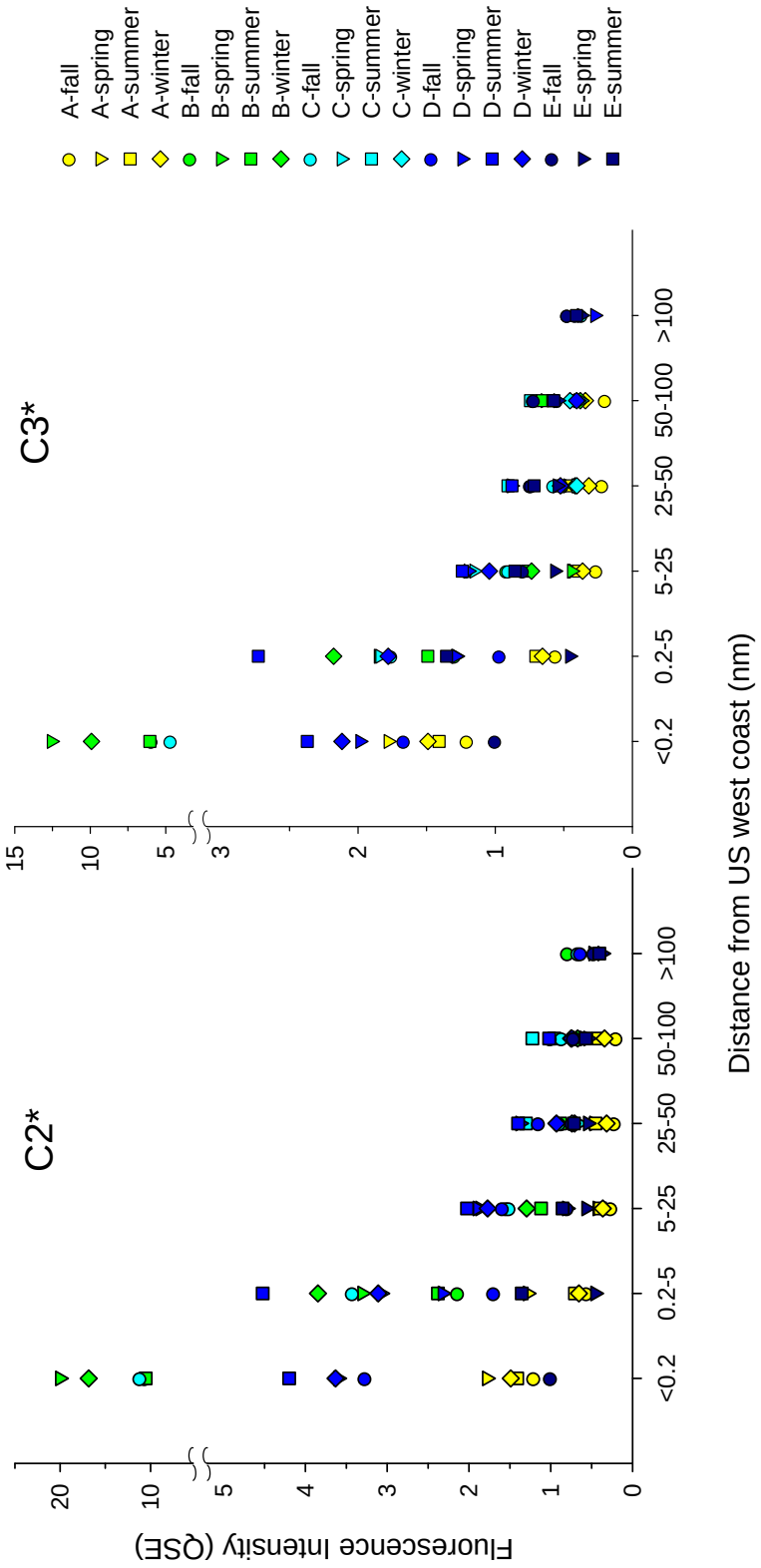

Figure 10. Seasonal changes in mean C2* and C3* concentrations, by zone (A–E; see Figure 1) and distance from the U.S. West Coast.

3.2.2 Western Pacific: Asian Ports

A statistical analysis of the effect of port and season on tracer concentrations indicates there were strong seasonal differences between Ba and CDOM concentrations in the four Asian ports, with the strength of the seasonal effect differing among the ports (Appendix G). Concentrations of these tracers were always higher in summer than in winter, except for CDOM in Kaohsiung, which did not change between the two surveys. Mean Ba concentrations varied between seasonal surveys by a factor of 2 for Hong Kong, 1.4 for Busan, 1.5 for Tokyo Bay and 1.5 for Kaohsiung. CDOM concentrations varied by a factor of approximately 1.6 for Hong Kong, 1.9 for Busan, and 2.3 for Tokyo Bay. Manganese and phosphorus concentrations were not seasonally variable in the Asian ports, except P in Tokyo Bay, which were higher by a factor of approximately 2.2 during the summer. [See also Appendices A–F, for detailed maps of tracer concentrations.]

Limited additional data were collected along a transect beginning in Tokyo Bay during two transpacific cruises. Concentrations of all tracers were seen to decline along these transects. For CDOM, local oceanic concentrations (0.4 to 1.1 QSE at C2*) were reached within 25 to 50 nmi of Tokyo Bay.

3.3 Probabilistic Assessment of Tracer Utility

The overall purpose of this study was to identify chemical tracers of BWE that possess detectably large differences between concentrations in port and oceanic waters that are consistent across regions and at all times of the year. It is evident that the magnitude of differences between port and ocean waters will depend in part upon the distance from land (i.e., where open ocean conditions begin). In this section, the probabilistic assessment was made to determine whether thresholds for each tracer that would allow coastal and oceanic seawater to be reliably distinguished. The project further examined the degree to which tracers are likely to discriminate seawater from the ocean versus that sourced from different distances from land. This issue is particularly relevant, since some coastal states require BWE of coastwise vessels as close as 50 nmi from land (CSLC, 2006; DEQ, 2001; WDFW, 2007), whereas transoceanic arrivals are expected to conduct BWE at least 200 nmi offshore (IMO 2004). It is therefore important to understand how differently interpreted BWE boundaries impact upon each tracer's ability to distinguish "coastal" from "oceanic" water, under their various definitions.

3.3.1 Cumulative Density Functions (CDF)

A preliminary assessment of whether it is possible to set a threshold that distinguishes between seawater samples sourced from different distances from shore can be made by examining of the Cumulative density functions (CDFs) for each source location. To construct each CDF, the data points were sorted from lowest to highest and assigned to evenly-spaced percentile values according to the number of data points in the set. The data are plotted as lognormal cumulative distribution functions on a probability scaled x-axis. Each point (x_i, y_i) on the graph shows the probability (x_i) that a measurement was equal to or below the corresponding concentration (y_i) on the y-axis. If a threshold can be defined which completely separates samples from two different source locations, it will divide their CDFs without intersecting either of them.

The CDF for CDOM tracer C3* in the eastern Pacific Ocean is provided in Figure 11A. It is possible to draw a straight line that completely divides the samples collected from <0.2 nmi from those collected at >100 nmi (solid blue line), indicating that it is theoretically possible to set a threshold for distinguishing between oceanic and port water. However, this is not the case for samples sourced farther than 0.2nmi from the coast. Assuming a threshold was set at the position of the blue line, it is apparent that about 15 percent

of samples obtained from 0.2–5nmi from the coast lie below the line and consequently overlap with the range for oceanic distributions. Similarly, about half the samples collected at 5–25 nmi lie below the line, increasing to 90 percent at 25–50 nmi. It can be concluded that in order for C3* to act as an exclusive ballast water tracer, BWE would need to take place >100 nmi from land. If BWE were permitted 50–100 nmi from land, a higher threshold would be needed to allow for potentially elevated coastal signals. However, if the threshold were raised above the highest concentrations measured at 50–100nmi (dotted blue line) then more than 20 percent of port samples would be indistinguishable from oceanic samples, as would the vast majority of coastal samples obtained from farther than 0.2 nmi from land.

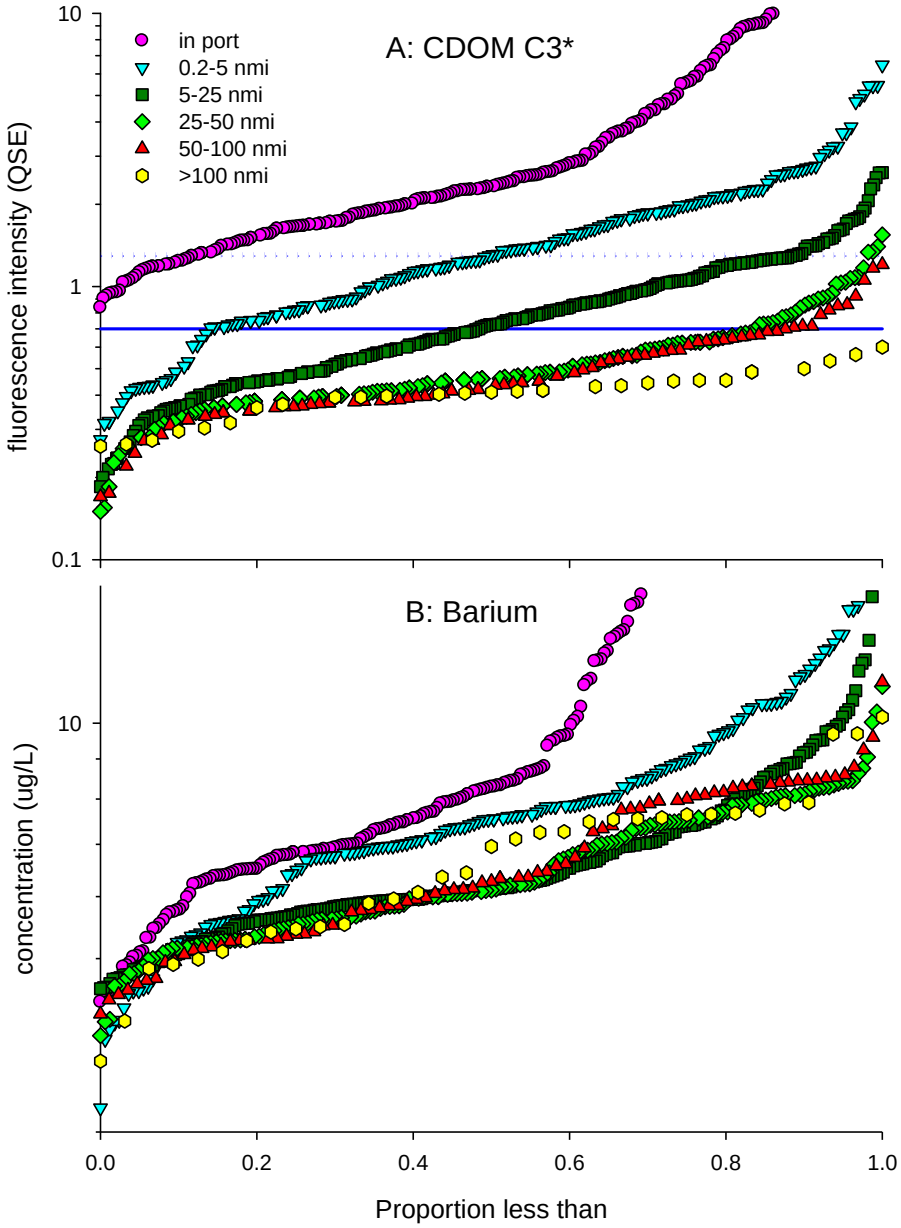

Figure 11. Cumulative density functions for A) CDOM tracer C3*, and B) Barium in samples collected at various distances from shore in the Pacific Ocean.

In sharp contrast, the CDF for barium in the eastern Pacific Ocean is provided in Figure 11B, indicating that it is impossible to draw a line that separates the data points associated with oceanic samples from port samples, or from any other group of samples. Thus, a simple univariate threshold for barium could not reliably distinguish between samples from exchanged vs. unexchanged ballast tanks in the Pacific Ocean.

The same conclusion can be drawn from the CDF for Ba and P, when considering data from the Asian ports (Figure 12). The performance of Mn in discriminating port from ocean sources is better, but this still shows considerable overlap (see next section for further analysis).

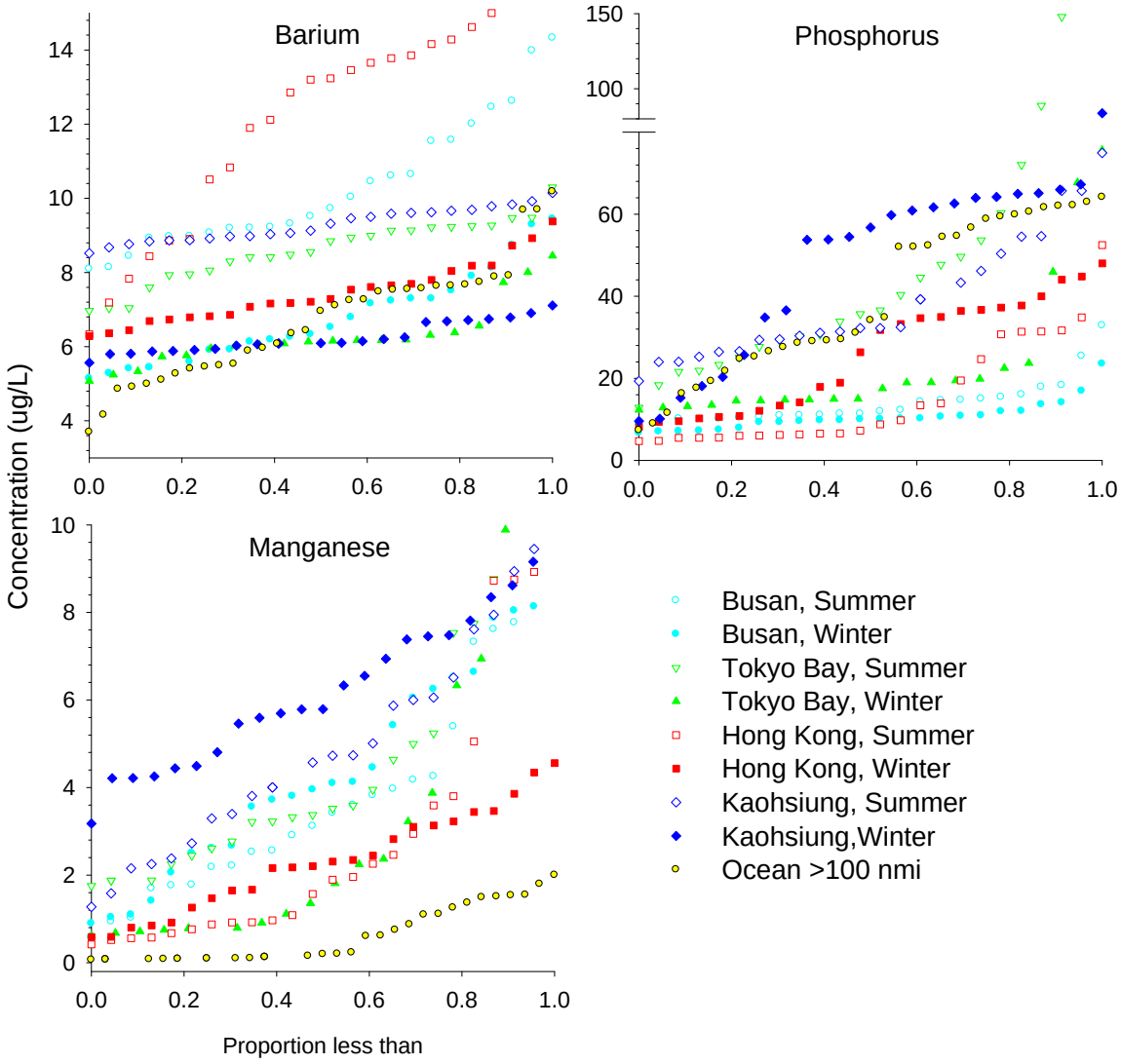

Figure 12. Cumulative density functions for barium, phosphorus and manganese in Asian port samples.

The CDFs for CDOM in the four Asian ports are provided in Figure 13. Whereas the vast majority of samples were above ocean concentrations, 10–20 percent of samples collected in winter surveys from Tokyo Bay and Busan were indistinguishable from oceanic concentrations.

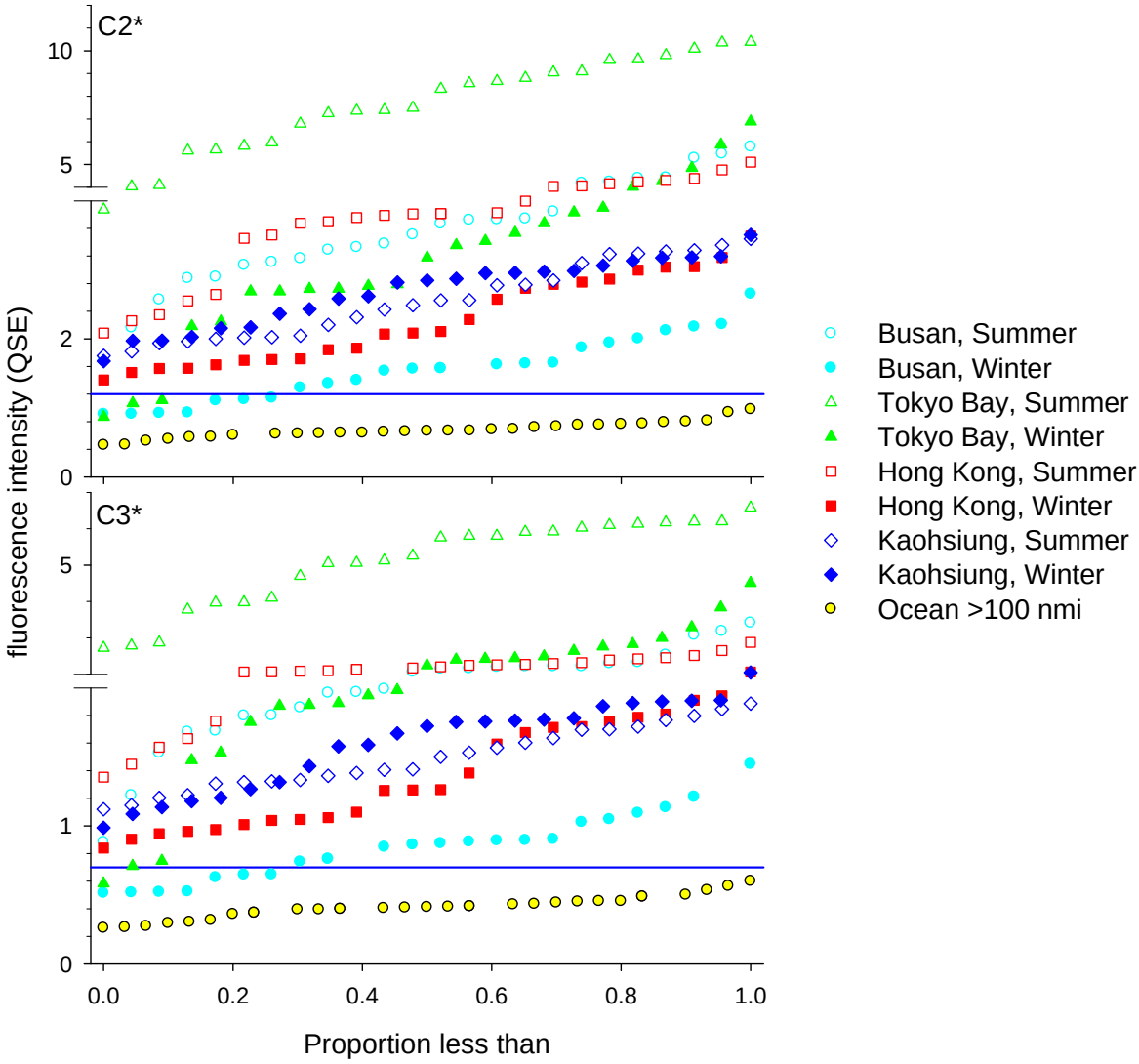

Figure 13. Cumulative density functions for C2* and C3* in Asian port samples.

3.3.2 Probability Density Functions (PDF)

Probability density functions (PDFs) are a graphical representation of the number or proportion of samples (y-axis) that are associated with a particular range of measured concentrations (x-axis). Each of the datasets was fitted to a PDF under the assumption of either normal or lognormal distributions, depending on which distribution achieved the better fit. Representations of fitted PDFs were generated using a Monte-Carlo simulation with 10,000 iterations, using the Matlab software (Mathworks Inc.). These were used to derive a PDF for the ratio of port:oceanic water for each tracer, in order to assess the probability of successfully distinguishing between oceanic and port samples using a particular tracer. This modeling was limited to data collected in the eastern North Pacific, where sampling coverage was most extensive.

Examination of the PDFs for the oceanic data collected during this study compared to previously published data for C3* (Murphy et al., 2006) revealed that the two datasets have different distributions (Figure 14). For C3, both datasets were approximately normally distributed with similar variances; however, the mean

concentration of C3* in the new dataset was approximately 0.25 QSE higher than in the prior dataset. It is presently unknown whether this difference can be attributed to inter-annual variation, analytical error, or other sources. It was therefore decided to proceed with the modeling of CDOM tracers using only the recent data to simulate oceanic tracer concentrations. This allowed modeling of the "worst-case scenario", since when background concentrations in the ocean are highest, the proportion by which tracer concentrations decrease as a result of BWE is lowest. For the trace elements, both datasets were statistically indistinguishable and all available data were used in the models.

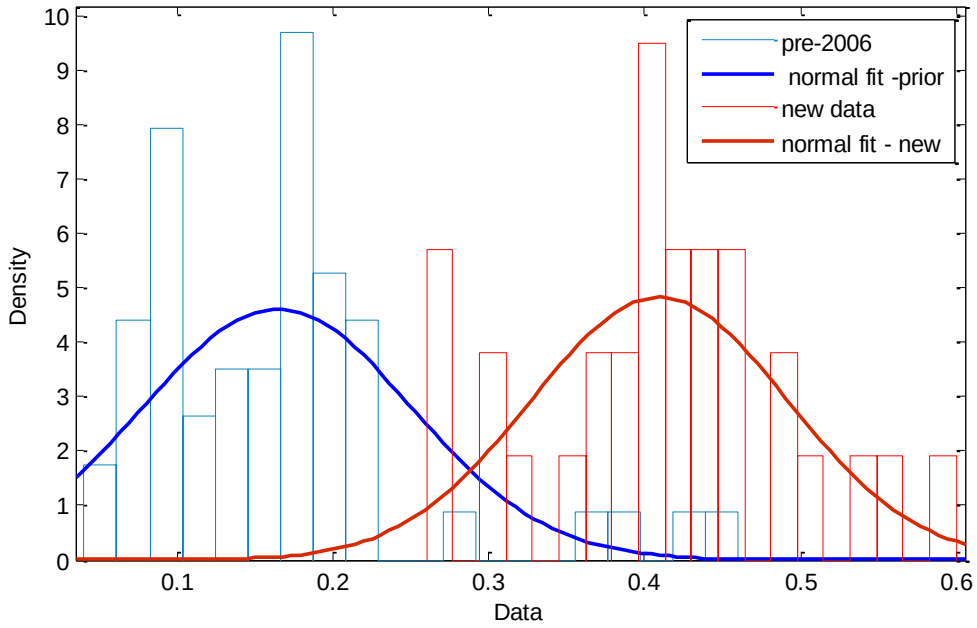

Figure 14. C3* probability density function for open ocean (>100 nmi) samples.

A preliminary assessment of parameter exclusivity can be made by inspecting the 5th and 95th percentiles of the simulated PDFs (Table 7). Tracers are considered exclusive when there is no overlap between the values of the 5th and 95th percentiles. By these criteria, C2* and C3* were exclusive to each of the oceanic and port water PDFs, whereas Ba, P and Mn were non-exclusive.

Table 7. Assessment of tracer exclusivity between port (<0.2nmi) and open ocean (>100 nmi) seawater, in samples from the eastern Pacific ocean.

		Modeled distribution	μ	σ	5th percentile	Mean	95th percentile	Exclusive
C3	Ocean	normal	0.41	0.08	0.27	0.41	0.54	YES
	Port	lognormal	1.1	0.81	0.8	4.2	11.8	
C2	Ocean	lognormal	-0.40	0.17	0.50	0.68	0.88	YES
	Port	lognormal	1.64	0.82	1.3	7.2	19.1	
Ba	Ocean	normal	5.8	1.6	3.1	5.8	8.5	NO
	Port	lognormal	2.3	0.6	4.0	12.3	27.4	
P	Ocean	lognormal	3.0	0.9	4.6	28.6	83.6	NO
	Port	lognormal	3.7	0.7	13.9	53.6	130.5	
Mn	Ocean	lognormal	-0.53	1.5	0.05	1.9	7.1	NO
	Port	lognormal	1.23	1.0	0.06	5.8	18.8	

A Monte-Carlo simulation was used to derive a PDF for the ratio of port:oceanic water for each of the parameters. The derived PDF for C3* is shown in Figure 15. The means and first percentiles for the PDF ratio of port:oceanic seawater for each of the tested parameters are presented in Table 8.

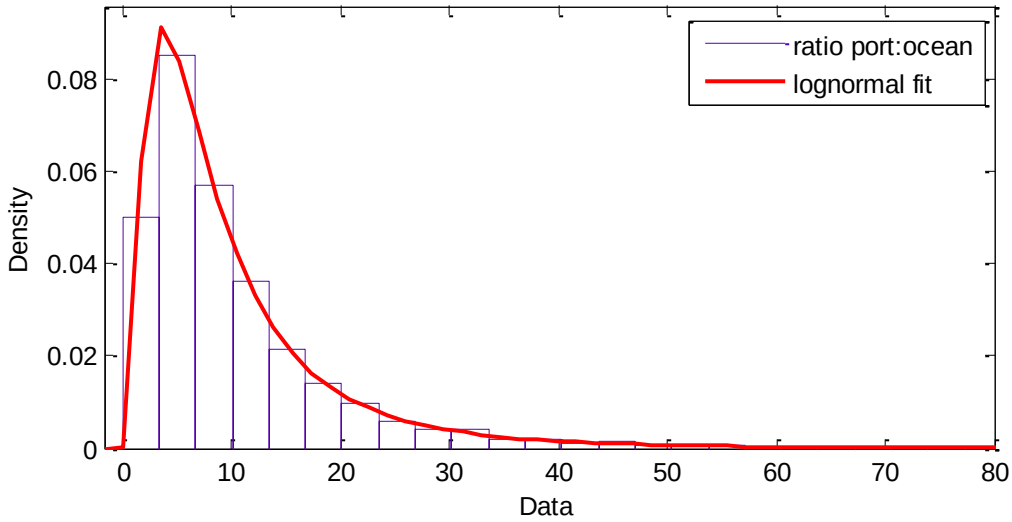

Figure 15. Simulated PDF for the ratio of port:oceanic seawater for CDOM tracer C3.

Table 8. Means and percentiles for PDF ratios of oceanic seawater (>100 nmi offshore) to port water (< 0.2 nm) on the U.S. West Coast.

Ocean / Port ratio	Mean	1st percentile	5th percentile	95th percentile
C3	10.6	1.1	1.9	29.6
C2	11.0	1.15	2.0	31.0
Ba	2.35	0.41	0.66	5.6
P	4.16	0.16	0.35	13.9
Mn	29.2	0.09	0.31	107

In order that a tracer can reliably distinguish between port and oceanic water, it is considered that the 1st percentile of the PDF ratio of port:oceanic seawater should be greater than 1.0. That is, for a pair of random samples consisting of one oceanic sample and one port sample, the tracer concentration should be greater for the port sample than for the oceanic sample in at least 99 percent of comparisons. If this ratio is less than 1.0, this would indicate that in at least 1 percent of comparisons, the concentration of a given tracer in the ocean sample would exceed its concentration in the port sample, corresponding to a "false positive" determination. By this criterion, CDOM tracers C2* and C3* were both reliable tracers with at least 99 percent of port:oceanic comparisons exceeding a ratio of 1.1, whereas Ba, P and Mn were unreliable. On average, it could be expected that the concentration of both C2* and C3* in a random port sample would be approximately 11 times greater than their concentrations in a random ocean sample.

4 DISCUSSION

4.1 Tracer Concentration and Distance from Shore

Predicting the change in a tracer's signal with distance from shore is critical to its potential success for verifying BWE. To define a global threshold for discriminating between samples from any two different sources, it must first be demonstrated that there is no significant degree of overlap between the concentrations of the tracer in the two source waters, regardless of the specific sites involved, or the time of year that sampling occurs. In this study, reliable discrimination between source waters was limited to CDOM tracers. For Ba, P and Mn, discrimination was hampered by very strong seasonal and geographical differences in tracer concentrations, occurring at both coastal and oceanic sites.

Earlier studies determined that for CDOM, there is a clear differentiation between its concentration in ballast water sourced from ports versus the open ocean (> 200 nmi from shore), supporting its use as a tool for verifying BWE by ships arriving to the U.S. from foreign ports, under current USCG regulations (Murphy et al., 2004b, 2006, 2007). However, the International Maritime Organization (IMO) and several state programs within the U.S. have recently begun to promote a 50 nmi limit for BWE for some vessel traffic, such as coastwise voyages (CSLC, 2006; DEQ, 2001; WDFW, 2007), creating a need to characterize the chemical differences between oceanic and coastal waters at a finer spatial resolution.

As in previous studies (Boehme et al., 2008; Murphy et al., 2007a), CDOM concentrations were highest within ports and very near to the coast, and decreased to oceanic levels at some distance from shore. The distance at which oceanic baseline concentrations occurred varied seasonally, regionally and along a north-south gradient. Over the entire study region, geographical rather than temporal factors were the major determinant of ambient CDOM concentrations near the coasts. CDOM concentrations in coastal regions can vary greatly in response to dynamic tidal circulation and large differences in seasonal freshwater inputs from regional river and estuary systems that border many ports.

Off the coast of southern California (Region A), CDOM concentrations were lowest overall, displaying short and steep decay functions. This trend reflects the relatively low CDOM concentrations within local port systems such as Los Angeles and Long Beach, which are located within highly engineered watersheds that drain arid regions, possessing both high salinities and restricted outflow of terrestrially-sourced organic material to the coast. Low coastal CDOM signals can be further attributed to rapid dilution of port water outflow via tidal mixing with low-CDOM, high-salinity seawater occurring in close proximity to land. The waters adjacent to northern California and the Pacific Northwest (Regions B–E) displayed more complex concentration profiles in coastal waters 0.2–50 nmi from shore, demonstrating seasonal shifts in the positions of oceanic water masses within the sampling regions and the presence of significant seasonal outflow from terrestrial sources, most significantly from the Straits of Juan de Fuca and the Columbia River.

The relatively elevated offshore CDOM concentrations in the Pacific Northwest and Gulf of Alaska indicate that BWEs performed <50 nmi from shore in these regions would run a significant risk of being determined non-compliant from a monitoring scheme based upon CDOM fluorescence, assuming no significant overlap with ocean values.

4.1.1 Distinguishing between Port (<0.2 nmi) and Oceanic (>100 nmi) Seawater

A minimum condition for chemical tracers to be suitable for BWE verification is a year-round ability to reliably discriminate between samples obtained from ports and samples obtained from oceanic waters beyond coastal influence. In this study, oceanic waters are defined as beginning at least 100 nmi from land. A definition based upon a 200 nmi boundary would have been consistent with current USCG regulations, but would have considerably reduced the number of oceanic samples available for comparison with port data; if anything, the approach taken in this study is conservative, as concentrations may be expected to decline slightly with increased distance from shore.

For CDOM tracers C2* and C3*, it was shown to be theoretically possible to set a concentration threshold that separates low-CDOM oceanic samples from high-CDOM port samples. Complete division was possible for port samples originating within 0.2 nmi from the U.S. West Coast, and within the ports of Hong Kong, and Koahsiung, whereas a small number of samples collected from the ports of Busan (Korea) and Tokyo Bay in winter overlapped with ranges in the open ocean. For Ba, P and Mn, any threshold set above the highest oceanic concentrations would also have exceeded concentrations in a large number samples originating in US and Asian ports. It can be concluded that none of the trace elements is individually sensitive enough to reliably discriminate between exchanged and unexchanged ballast water even if BWE were conducted in the open ocean according to current USCG requirements.

A statistical model of the ratio of port to oceanic seawater concentration in the eastern North Pacific predicts that for a pair of random samples consisting of one oceanic sample and one port sample, CDOM concentrations would on average be more than 10 times greater in the port sample, and would be greater for the port sample than for the oceanic sample in more than 99 percent of comparisons. It should be recognized that this prediction is specific to this dataset, which was based upon data from ports on the U.S. West Coast and a relatively small number of oceanic sites, sampled over a limited period of time. Inclusion of data for a larger number of ports, together with more extensive samples from the open ocean, will improve the reliability of statistical models.

4.1.2 Distinguishing between Port (<0.2 nmi) and Coastal (>50 nmi) Seawater

An ability to distinguish between port samples and coastal samples obtained farther than 50 nmi from land would be critical to verifying BWE when performed in compliance with state ballast water management regulations, which allow BWE at any distance beyond the 50 nmi coastal boundary (CSLC, 2006; DEQ, 2001; WDFW, 2007). Environmental tracer distributions in this study indicate that chemical tracer verification of coastal BWE would be challenging, as uniform discrimination of this boundary across the entire U.S. West Coast was not supported by any tracer studied, including salinity. The persistence of elevated coastal CDOM signals farther than 50 nmi from the northerly U.S. states and Canada implies the possibility of establishing another regional threshold for CDOM identifying coastal BWE in this area. However, enforcement efforts would need to consider more explicitly seasonal variability in the CDOM decay function and north to south range of elevated coastal CDOM, in defining operational thresholds for compliance.

4.1.3 Distinguishing between Near-Shore (<50 nmi) and Oceanic (>100 nmi) Seawater

To detect ships that conduct BWE unacceptably close to shore, it must be possible to discriminate between oceanic samples and coastal samples obtained nearer to land. Due to regional and temporal variations in the penetration of coastal tracer signals, none of the tracers studied could do this consistently for eastern Pacific samples. For CDOM, despite a general trend of decreasing concentration with increasing distance from

land, there was significant overlap between the ranges of concentrations observed at successive distances from shore. For example, approximately four-fifths of all samples collected at distances of 25–100 nmi from the coast, half the samples collected 5–25 nmi from the coast, and an eighth of samples collected within 5 nmi, had concentrations overlapping with ranges observed in the open ocean (>100 nmi). This indicates that while some ships conducting BWE outside of designated zones could be detected due to higher-than-expected CDOM concentrations, many would not. Furthermore, the rate of successfully detecting noncompliant BWE would be expected to decrease rapidly the farther offshore that BWE were performed.

4.2 Setting Thresholds for Verifying BWE

Murphy et al. (2006) proposed thresholds for verifying ballast water using CDOM, based solely upon C2* and C3* measurements in ballast tanks. The results of this and parallel studies on the distribution of CDOM in ports and the ocean will generate a large dataset which in the future can be used to independently assess the appropriateness of these thresholds. This assessment must take account of the fact that due to a combination of factors, ballast tanks can retain a significant coastal signal following BWE. Previous research has found that ships can demonstrate a wide range of BWE efficiencies when attempting to exchange precisely 95 percent of the tank volume, especially when using the Flow-Through method (Murphy et al., 2004a; Ruiz et al., 2005).

5 CONCLUSIONS/RECOMMENDATIONS

This study examined the distribution of ballast water tracers along eastern and western rim coasts of the North Pacific Ocean. It has been established that CDOM fluorescence intensity can reliably differentiate seawater samples collected in ports from seawater obtained from the open ocean more than 100 nmi from land, at minimum for the U.S. and Asian ports sampled in this study (U.S.: Los Angeles/Long Beach, San Francisco, San Diego, Portland, Puget Sound; Asia: Busan, Hong Kong, Kaohsiung, Tokyo Bay). This was in contrast to the three trace elements (Ba, P, and Mn), which did not consistently discriminate port from ocean samples. It has further been demonstrated that due to seasonally and geographically variable CDOM signals in coastal waters, it would not be possible to reliably determine the distance from land that BWE took place using only fluorescence data.

However, from an environmental perspective, the most important objective is to identify the vessels with the unexchanged port water, as these present a much greater risk than even water ballasted a mile offshore, because larval densities decrease dramatically with distance from source due to dilution. A recent study (Dunstan and Bax, 2008) modelled invasion risk of Asterias Amurensis (invasive seastar in Australia) and ballast water exchange, and concluded that BWE decreased invasion risk but it did not really matter how far offshore BWE was done, because larval densities decline so rapidly once outside of an embayment. So, the corollary is that CDOM will be capable of detecting vessels that did not exchange its ballast water. Vessels conducting exchange nearshore (< 50 nautical miles from land) would have an increased chance of being identified as noncompliant due to elevated concentrations of CDOM, but more research into seasonal and geographic variability would be needed to determine the risk. However, the vessels that did BWE but did not do it in compliance with distance-from-shore regulations represent a far lesser invasion risk than those that did not conduct any exchange. Thus, it is recommended to use CDOM to augment the current BWE verification method by identifying the high risk group of noncompliant vessels.

The preliminary indications from a statistical model showed that oceanic and port seawater could be successfully distinguished by CDOM concentration. This suggests that routine application for this purpose is feasible. To refine this model, it is recommended that more data be collected to formally examine the effects of specific threshold concentrations and offshore distances in the application of CDOM concentration for BWE verification.

In particular, the distribution and variability of CDOM in the open ocean must be well characterized and BWE thresholds set high enough that no ship that conducts BWE in designated exchange areas with at least 95 percent efficiency is flagged as non-complying due to the presence of higher-than-expected tracer concentrations in its ballast tanks. In addition, better guidelines on the best-practice implementation of BWE under current technology are needed to ensure that ships know how to complete BWE effectively, and so that enforcement efforts are appropriately directed.

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APPENDIX A. REGIONAL MAPS FOR CONSERVATIVE TRACERS SALINITY AND MOLYBDENUM

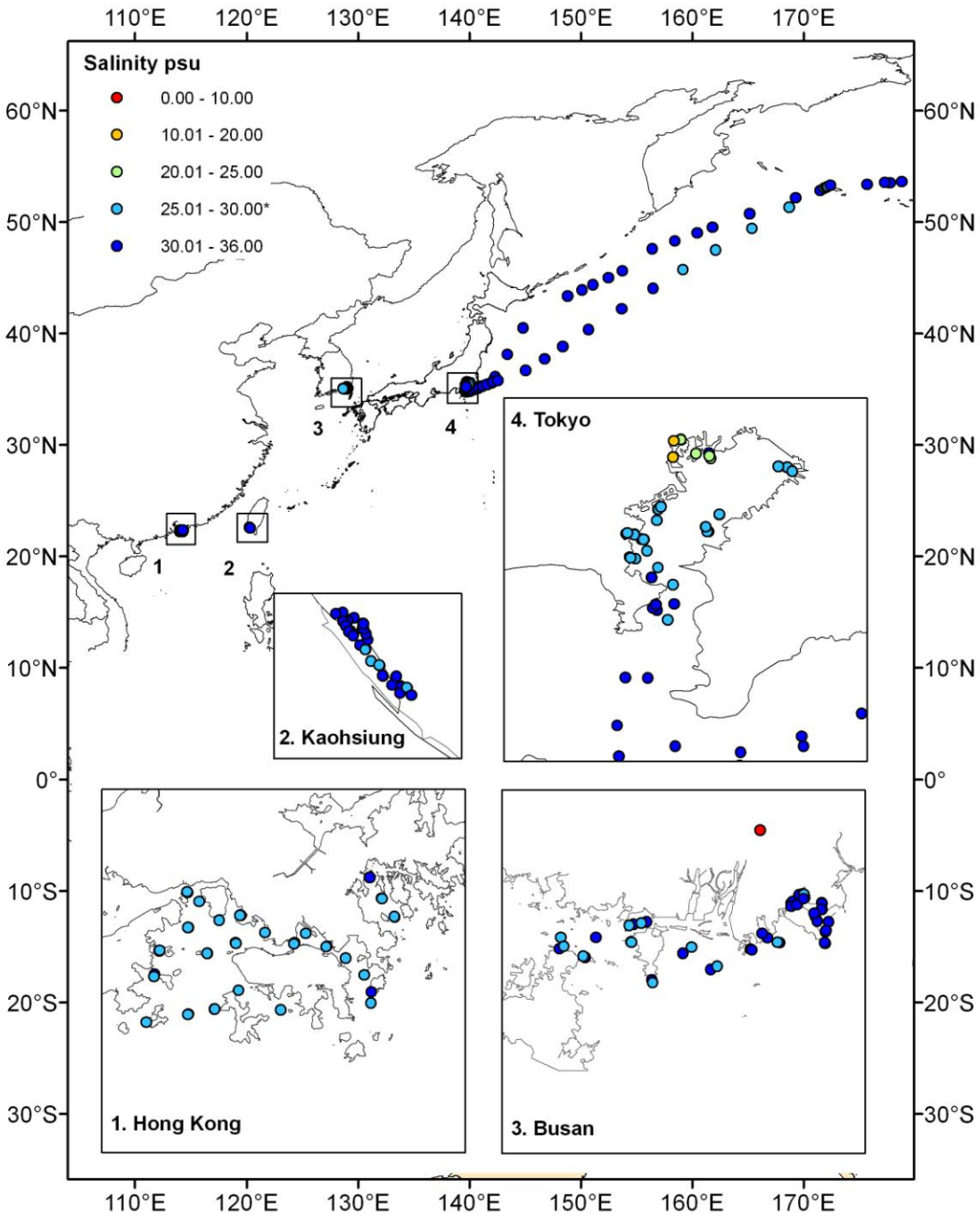

Figure A-1. Salinity distribution in the western north Pacific during this study.

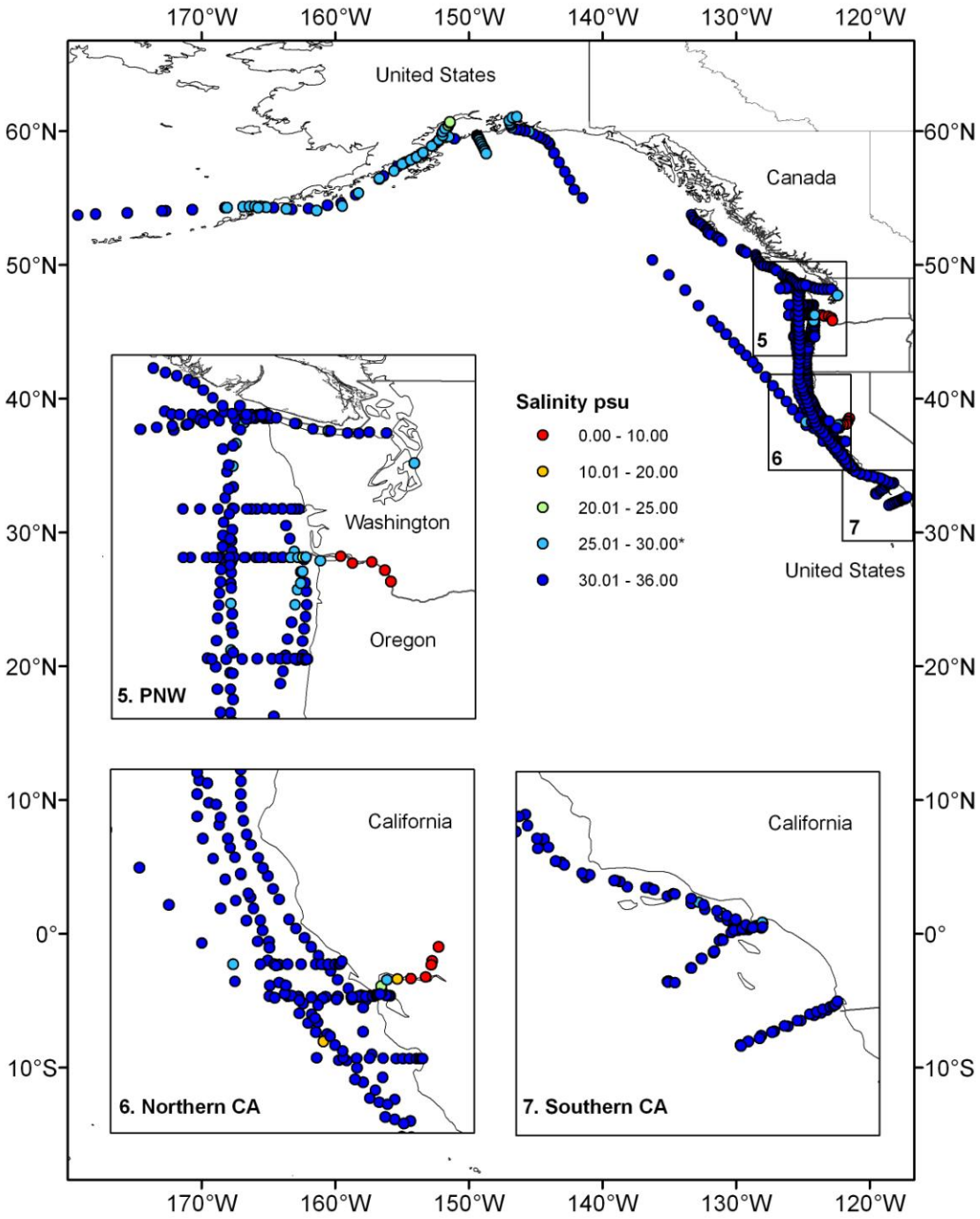

Figure A-2. Salinity distribution in the eastern north Pacific during this study.

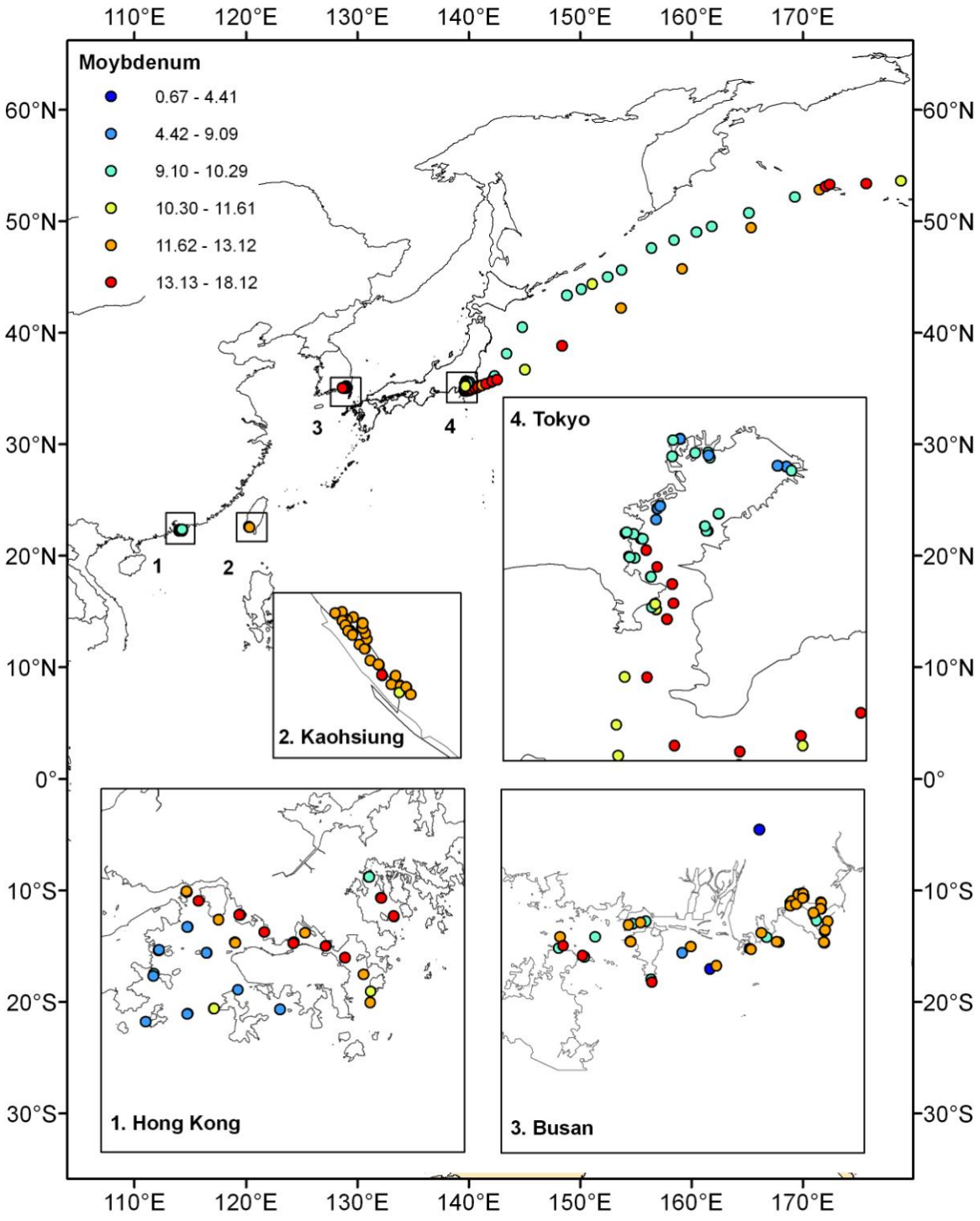

Figure A-3. Molybdenum distribution in the western north Pacific during this study.

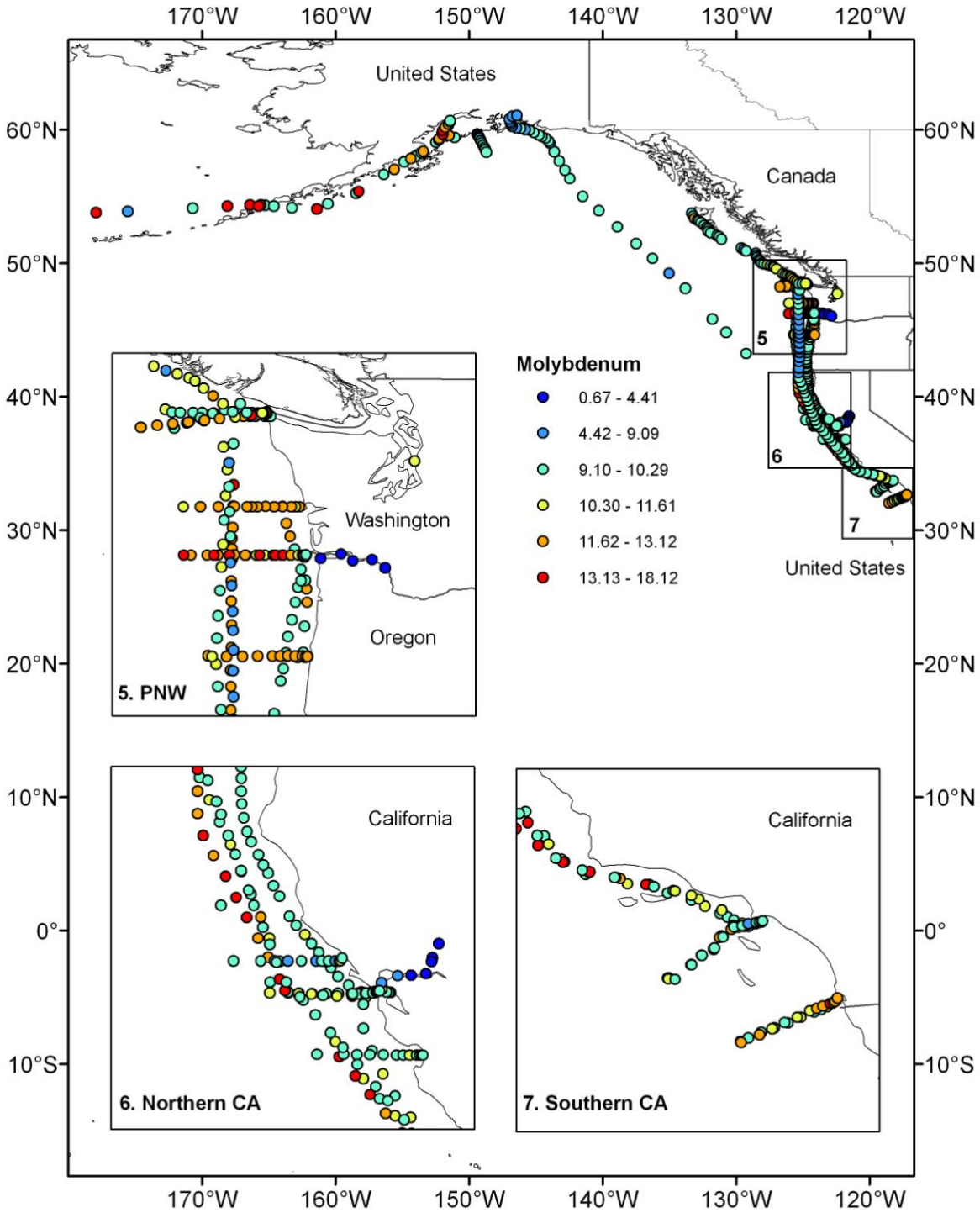

Figure A-4. Molybdenum distribution in the eastern north Pacific during this study.

APPENDIX B. REGIONAL MAPS FOR BWE TRACER: BARIUM

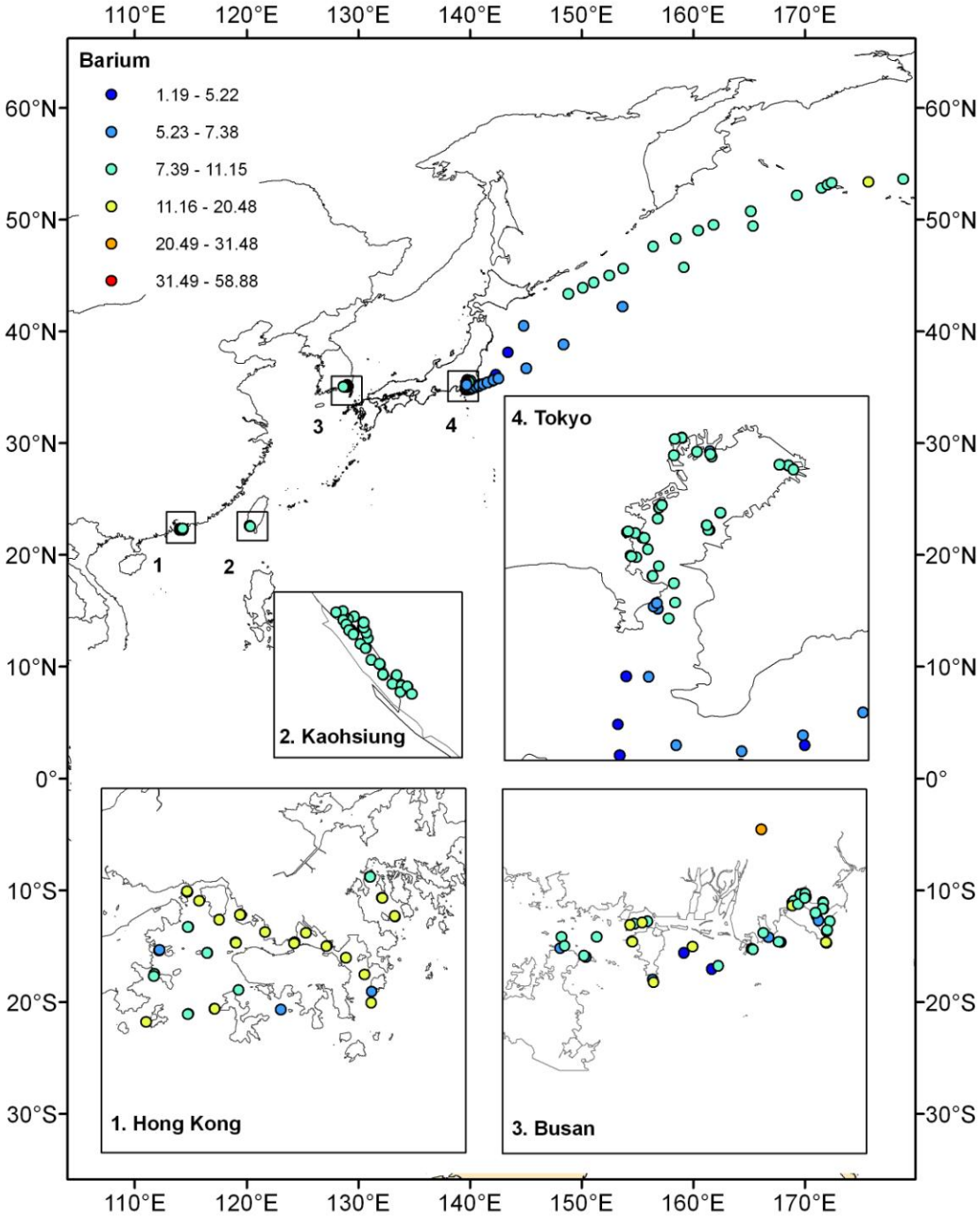

Figure B-1. Barium distribution in the western north Pacific during this study.

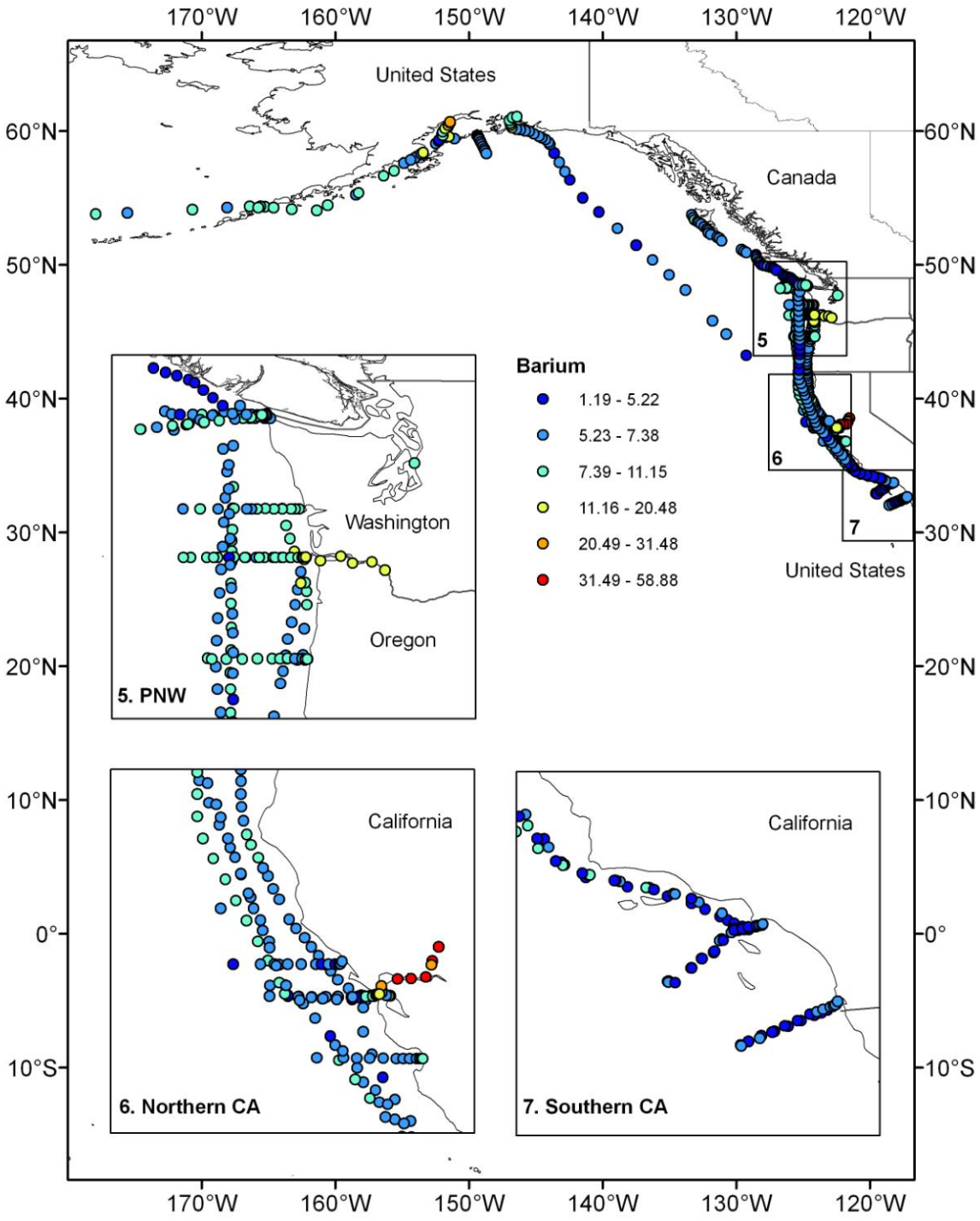

Figure B-2. Barium distribution in the eastern north Pacific during this study.

APPENDIX C. REGIONAL MAPS FOR BWE TRACER: PHOSPHORUS

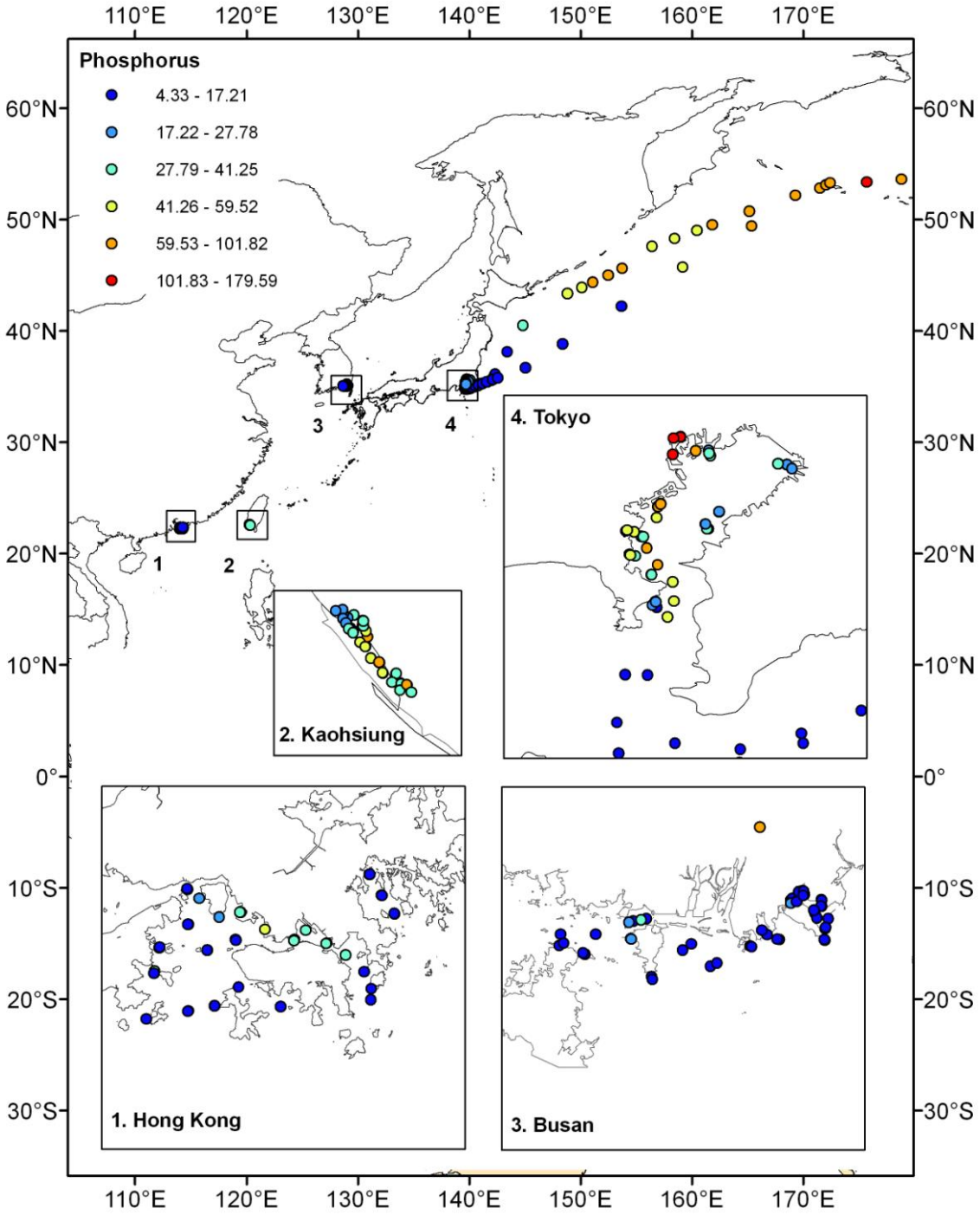

Figure C-1. Phosphorus distribution in the western north Pacific during this study.

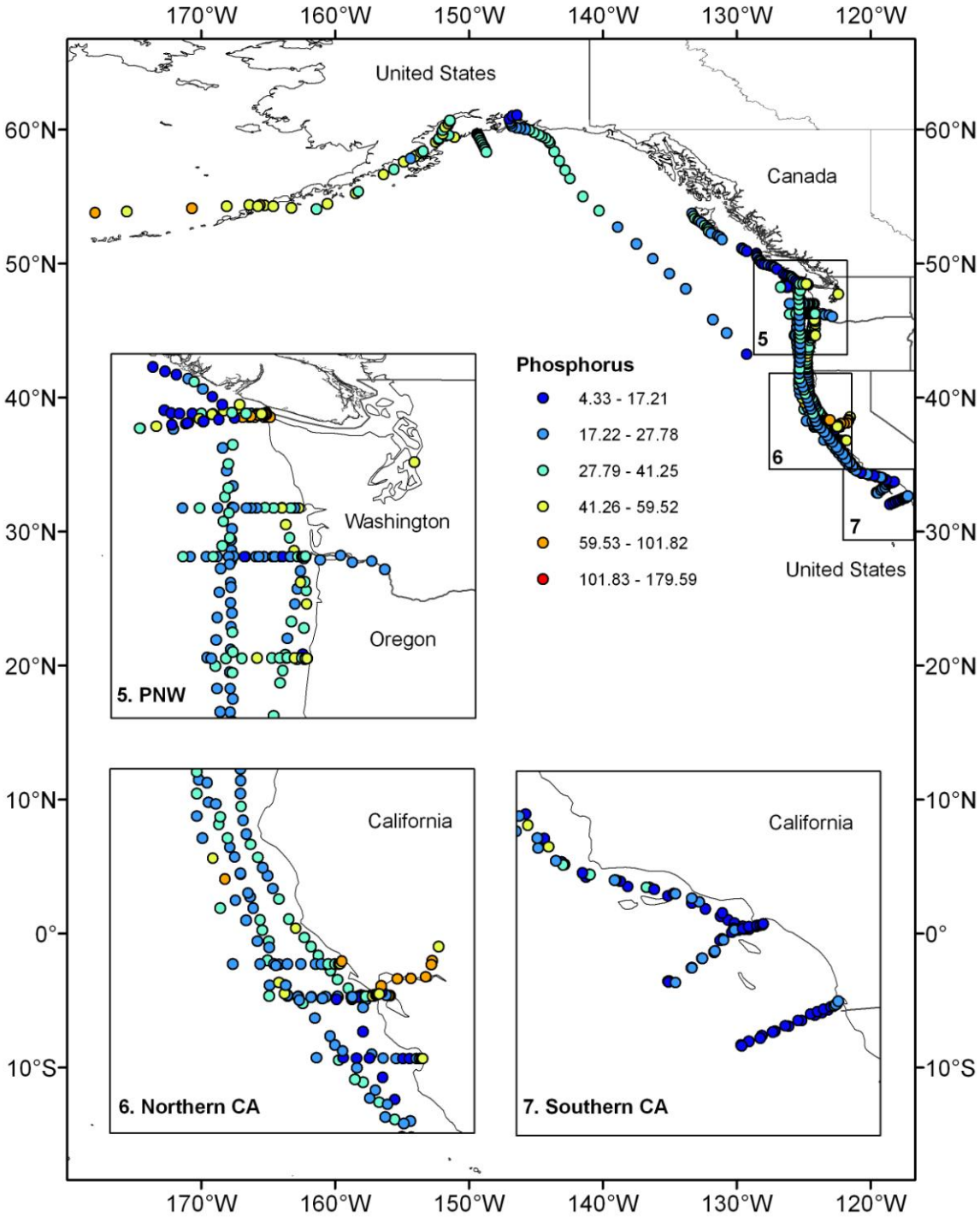

Figure C-2. Phosphorus distribution in the eastern north Pacific during this study.

APPENDIX D. REGIONAL MAPS FOR BWE TRACER: MANGANESE

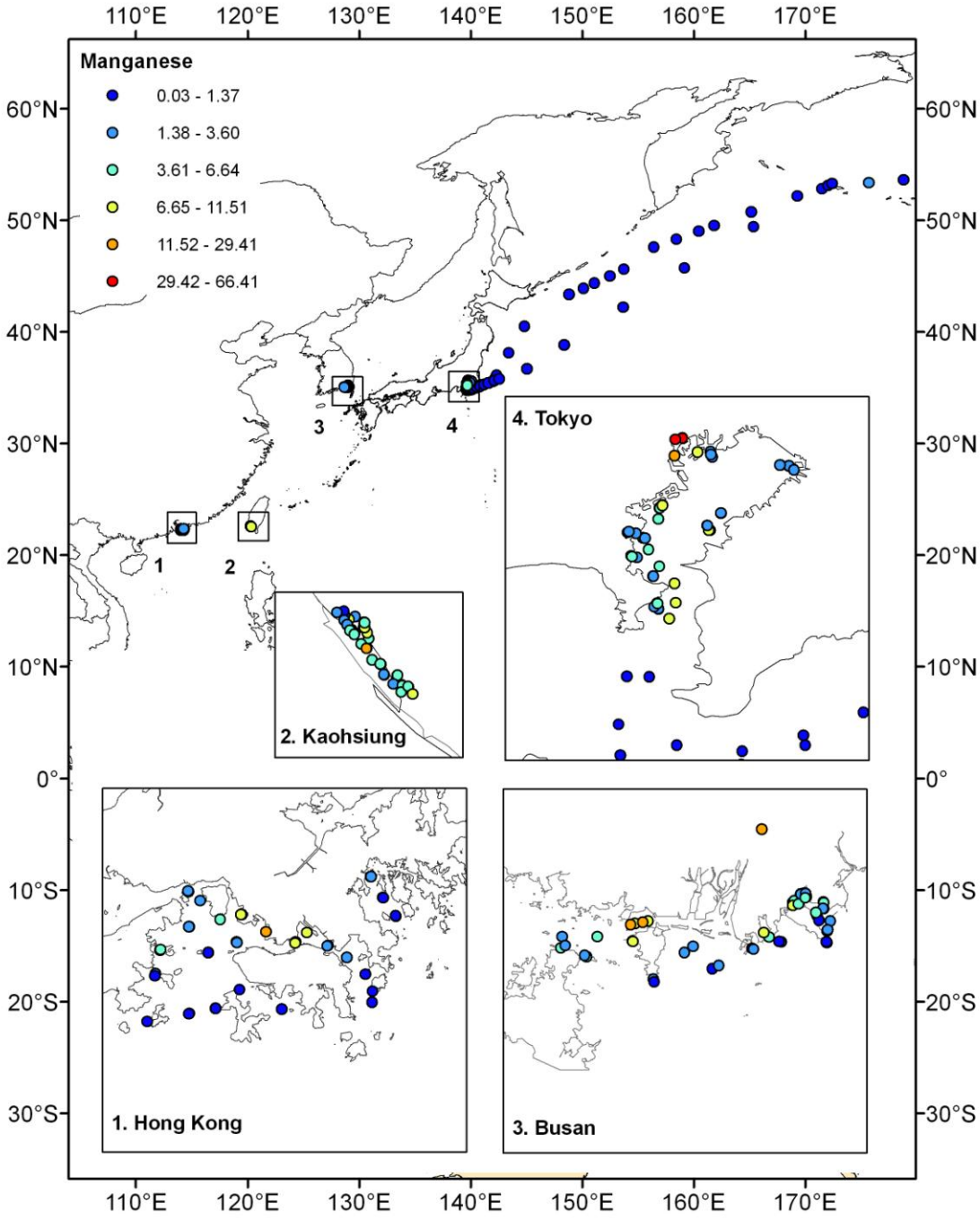

Figure D-1. Manganese distribution in the western north Pacific during this study.

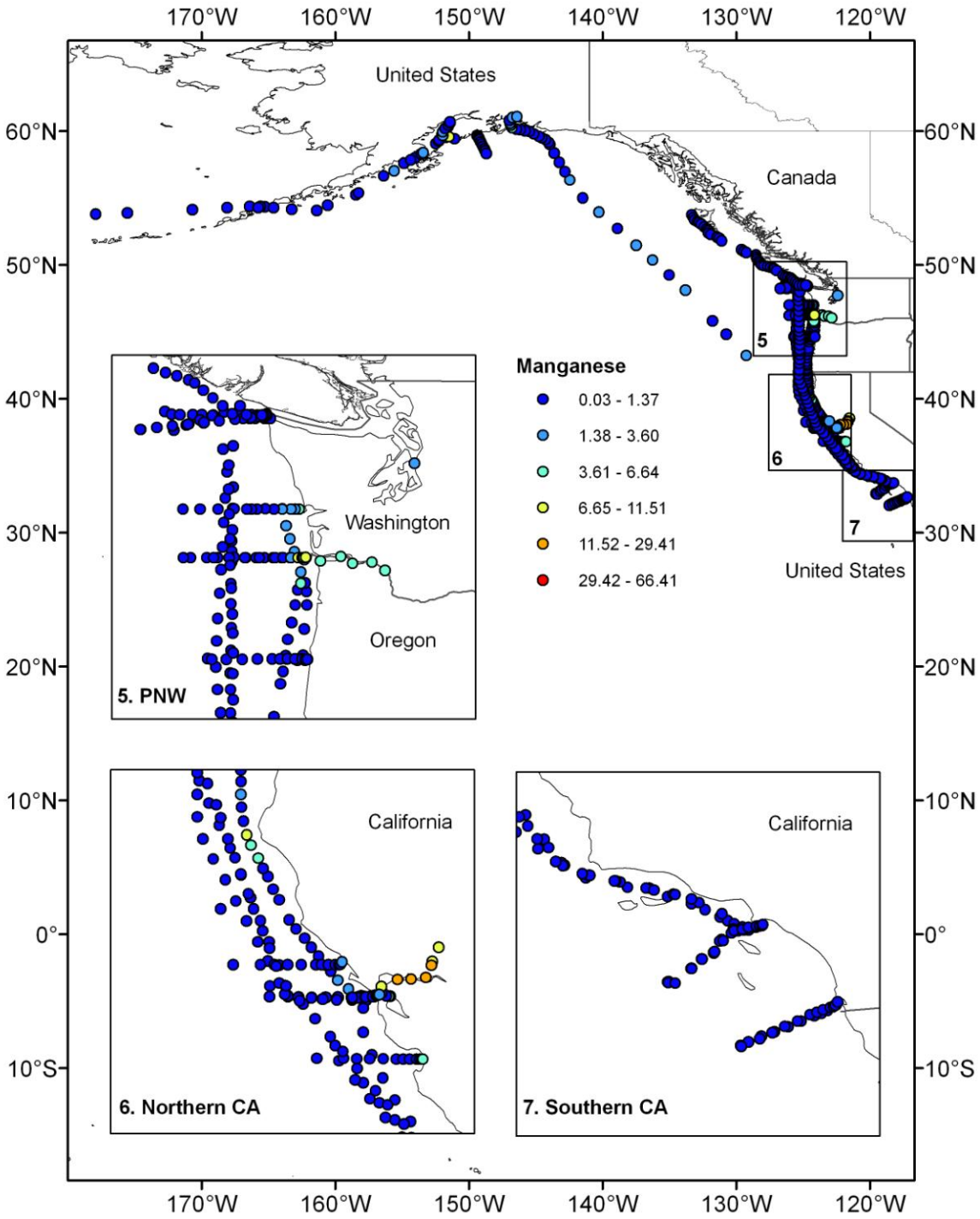

Figure D-2. Manganese distribution in the eastern north Pacific during this study.

APPENDIX E. REGIONAL MAPS FOR BWE TRACER: C2*

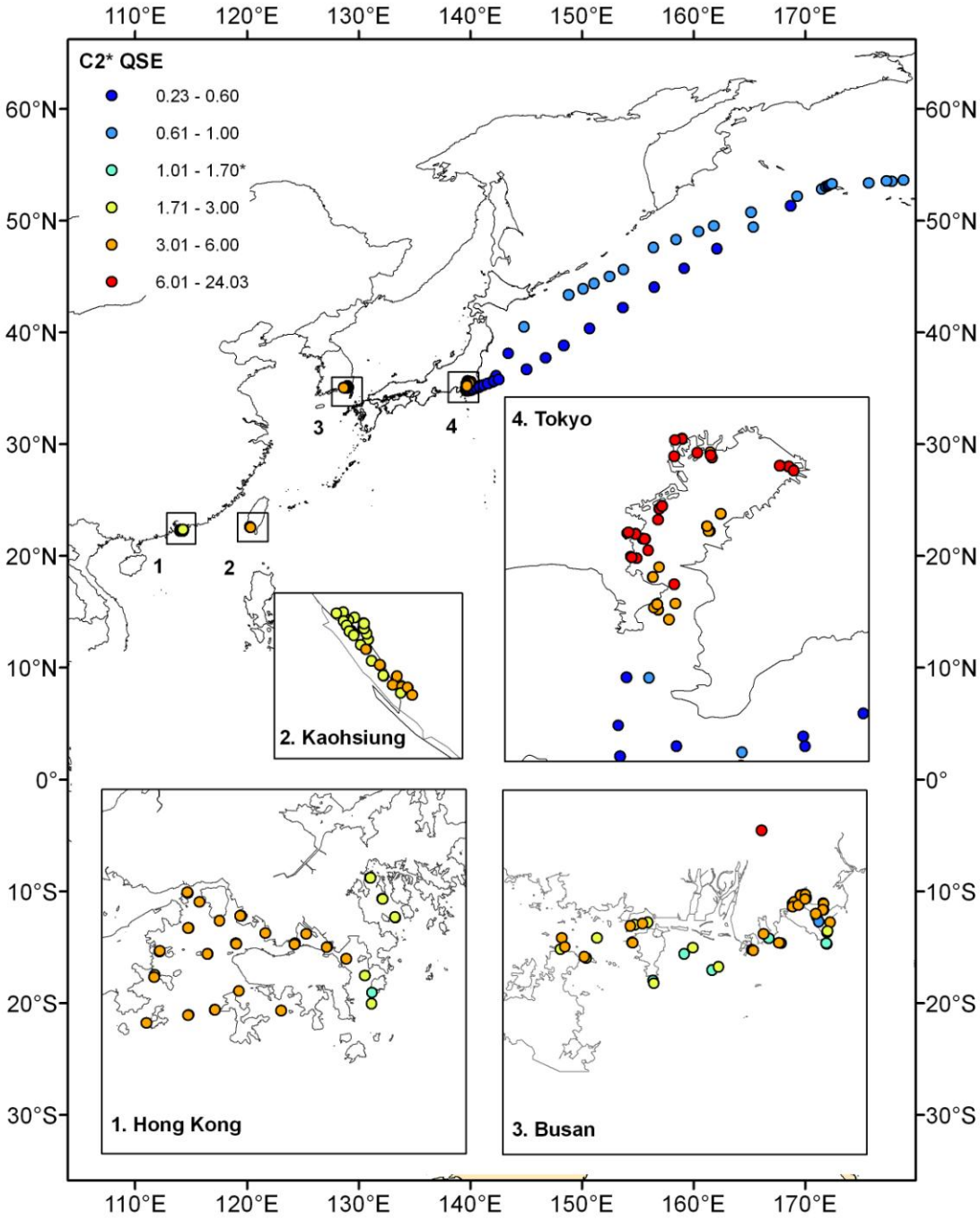

Figure E-1. C2* distribution in the western north Pacific during this study.

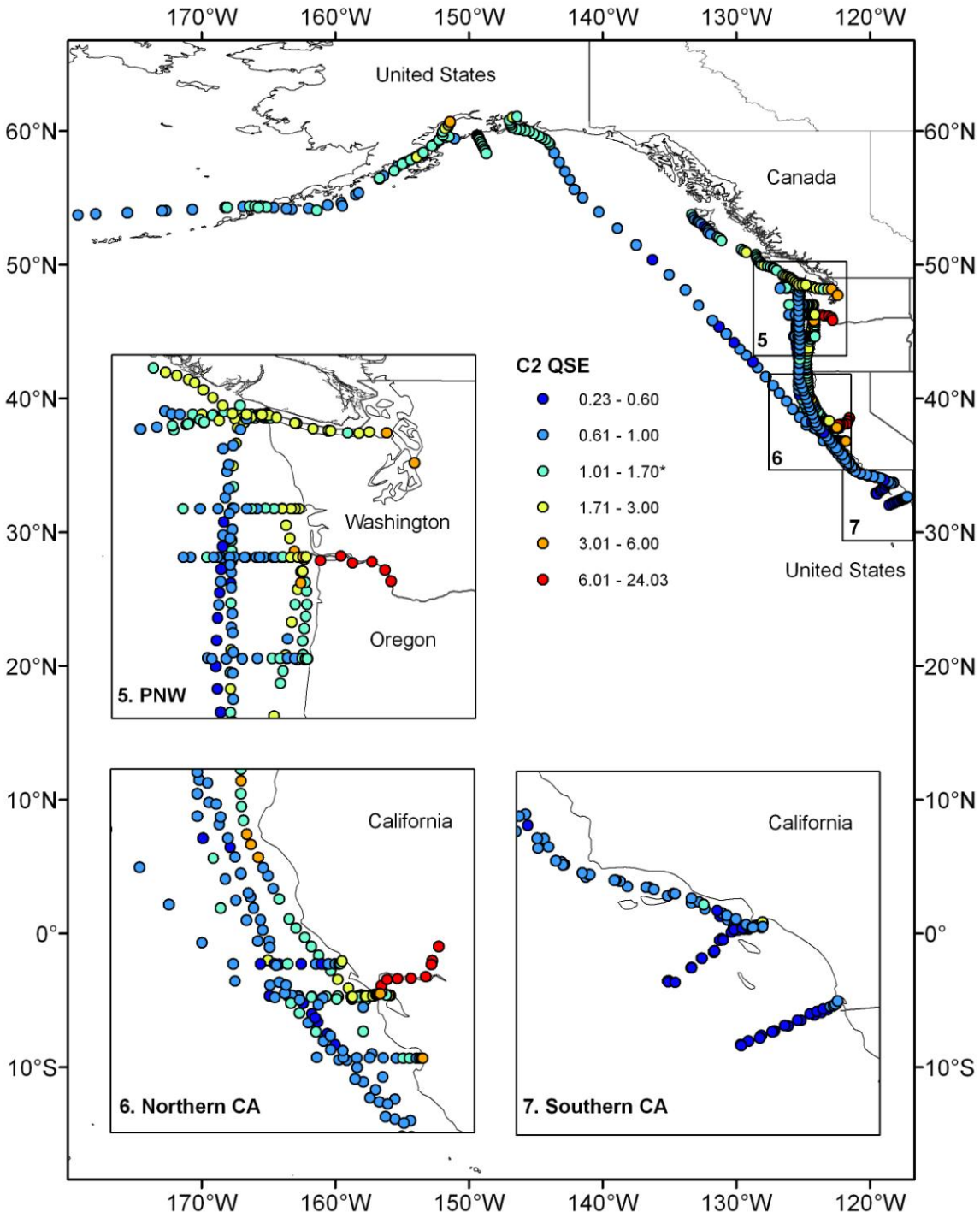

Figure E-2. C2* distribution in the eastern north Pacific during this study.

APPENDIX F. REGIONAL MAPS FOR BWE TRACER: C3*

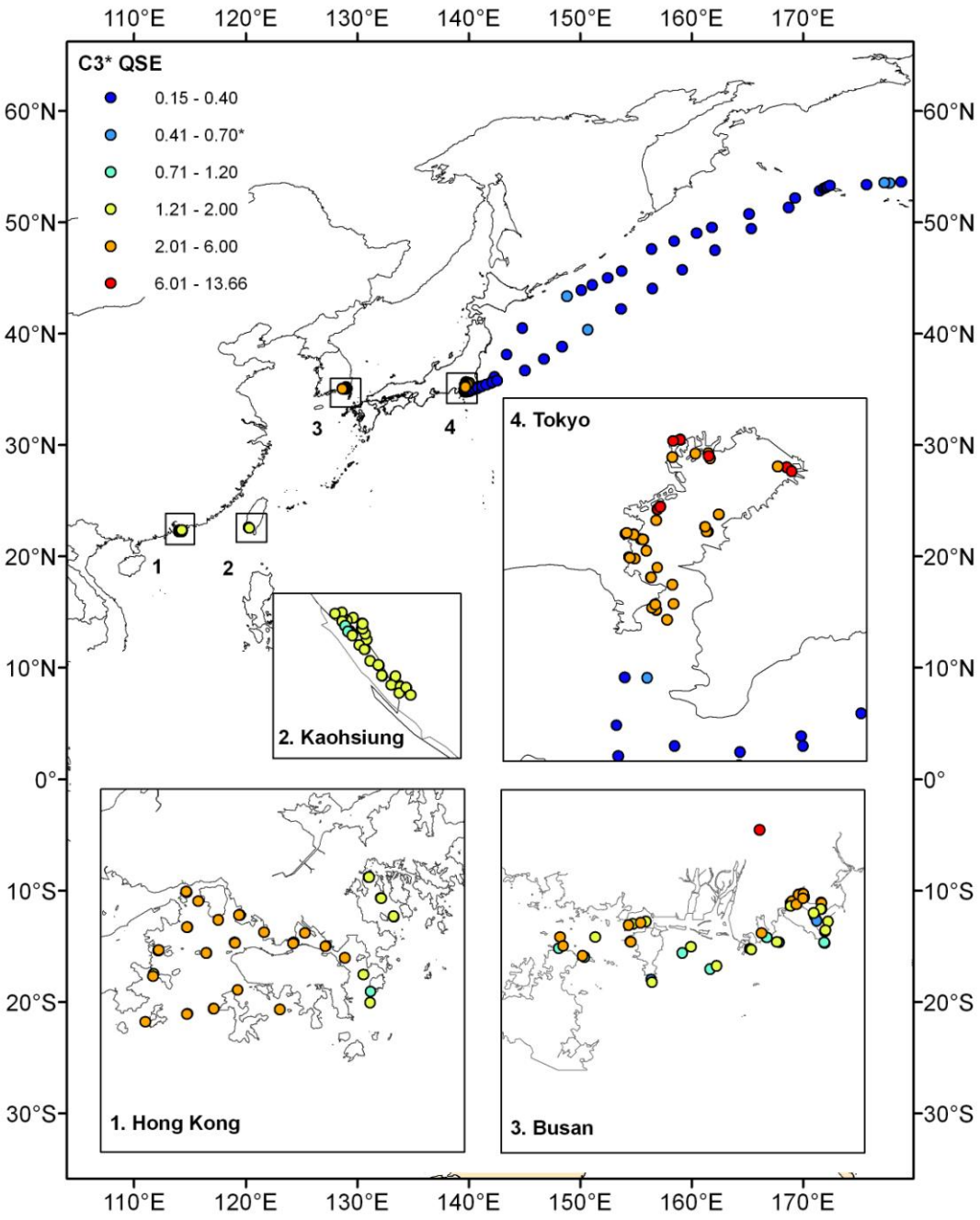

Figure F-1. C3* distribution in the western north Pacific during this study.

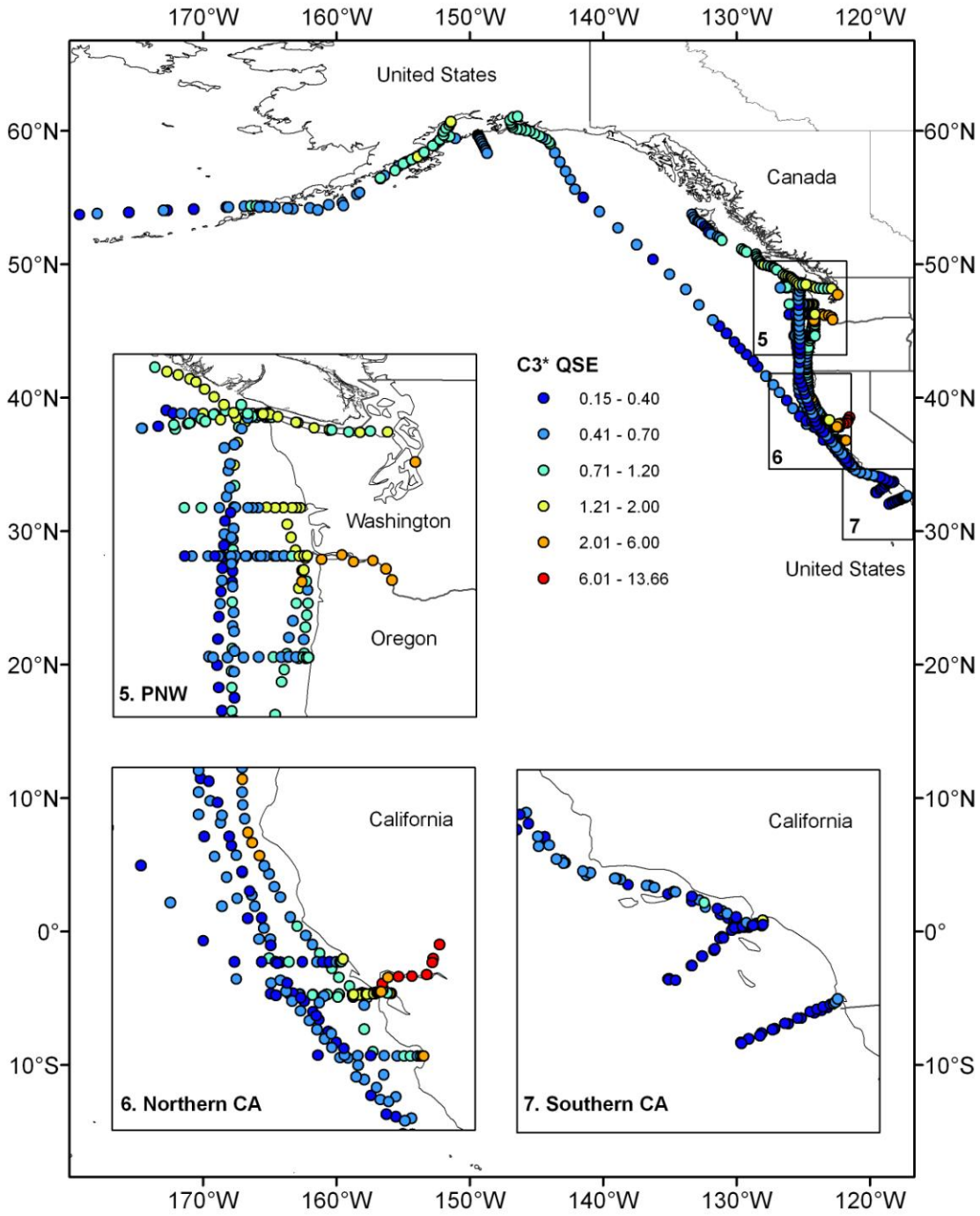

Figure F-2. C3* distribution in the eastern north Pacific during this study.

APPENDIX G. STATISTICAL RESULTS

Table G-1. T-test for differences between mean concentrations of CDOM: foreign ports vs. open ocean. Concentrations were log-transformed prior to analysis.

Port	Variable	t	DF	Prob	Variable	t	DF	Prob
TW-p-win	logC2	24.24	72	<.0001	logC3	21.61	72	<.0001
TW-p-sum	logC2	23.16	73	<.0001	logC3	27.29	71.5	<.0001
HK-p-win	logC2	19.31	73	<.0001	logC3	18.07	73	<.0001
HK-p-sum	logC2	28.55	73	<.0001	logC3	31.73	65.6	<.0001
JP-p-win	logC2	13.86	27	<.0001	logC3	14.99	28.5	<.0001
JP-p-sum	logC2	37.06	73	<.0001	logC3	37.25	73	<.0001
KR-p-win	logC2	12.84	73	<.0001	logC3	11.36	73	<.0001
KR-p-sum	logC2	26.76	73	<.0001	logC3	24.07	73	<.0001

Table G-2. Summary statistics for CDOM concentrations in Kaohsiung, Busan, Tokyo Bay and Hong Kong. Concentrations were log-transformed prior to analysis.

Tracer	Survey	N	Mean	s	CL	SD	s	CL	Minimum	Maximum	exp(Mean)
logC2	TW-p-win	23	0.97	±	0.09	0.20	±	0.05	0.52	1.26	2.63
logC3	TW-p-win	23	0.44	±	0.09	0.21	±	0.05	-0.01	0.72	1.56
logC2	TW-p-sum	24	0.92	±	0.09	0.22	±	0.05	0.56	1.24	2.50
logC3	TW-p-sum	24	0.39	±	0.07	0.16	±	0.04	0.11	0.64	1.47
logC2	HK-p-win	24	0.78	±	0.12	0.28	±	0.07	0.34	1.25	2.19
logC3	HK-p-win	24	0.28	±	0.12	0.29	±	0.07	-0.17	0.72	1.32
logC2	HK-p-sum	24	1.28	±	0.10	0.24	±	0.06	0.73	1.63	3.58
logC3	HK-p-sum	24	0.75	±	0.08	0.19	±	0.04	0.30	1.06	2.11
logC3	JP-p-win	23	0.70	±	0.22	0.51	±	0.12	-0.55	1.51	2.00
logC2	JP-p-win	23	1.07	±	0.22	0.51	±	0.12	-0.14	1.93	2.92
logC3	JP-p-sum	24	1.59	±	0.11	0.27	±	0.06	1.00	1.88	4.92
logC2	JP-p-sum	24	1.99	±	0.13	0.30	±	0.07	1.35	2.34	7.35
logC2	KR-p-win	24	0.39	±	0.13	0.31	±	0.07	-0.09	0.97	1.48
logC3	KR-p-win	24	-0.19	±	0.13	0.30	±	0.07	-0.67	0.37	0.82
logC2	KR-p-sum	24	1.26	±	0.12	0.28	±	0.07	0.52	1.75	3.52
logC3	KR-p-sum	24	0.70	±	0.12	0.29	±	0.07	-0.13	1.23	2.02
logC2	oceanref	51	-0.47	±	0.07	0.25	±	0.04	-1.31	-0.02	0.63
logC3	oceanref	51	-1.01	±	0.08	0.29	±	0.05	-1.90	-0.51	0.36

Table G-3. ANOVA: Effect of port and season on CDOM concentrations in Kaohsiung, Busan, Tokyo Bay and Hong Kong. Concentrations were log-transformed prior to analysis.

Name	Source	DF	SS	F	Prob
logC2	port	3	14.21	51.17	4.94E-24
logC2	season	1	14.82	160.08	9.89E-27
logC2	port*season	3	7.10	25.56	7.59E-14
logC2	ERROR	182	16.85		
logC3	port	3	22.08	85.74	1.26E-34
logC3	season	1	14.60	170.08	7.06E-28
logC3	port*season	3	7.25	28.15	5.3E-15
logC3	ERROR	182	15.62		

Table G-4. ANOVA: Effect of port and season on trace element concentrations in Kaohsiung, Busan, Tokyo Bay and Hong Kong. Concentrations were log-transformed prior to analysis.

Name	Source	DF	SS	F	Prob
logBa	port	3	1.68	15.26	0.00000
logBa	season	1	7.57	206.09	0.00000
logBa	port*season	3	0.14	1.25	0.29188
logBa	ERROR	181	6.65		
logMn	port	3	24.21	12.56	0.00000
logMn	season	1	0.33	0.52	0.47371
logMn	port*season	3	8.84	4.59	0.00404
logMn	ERROR	181	116.29		
logP	port	3	41.87	42.16	0.00000
logP	season	1	0.17	0.52	0.47196
logP	port*season	3	12.69	12.78	0.00000
logP	ERROR	181	59.92		

Table G-5. T-test for differences between mean concentrations of trace elements: foreign ports vs. open ocean. Concentrations were log-transformed prior to analysis.

Ttest	Variable	tValue	DF	Probt	Variable	tValue	DF	Probt	Variable	tValue	DF	Probt
TW-p-win	logBa	-1	38.7	0.3231	logMn	13.14	36.9	<.0001	logP	1.16	54	0.2498
TW-p-sum	logBa	8.31	35.5	<.0001	logMn	10.72	48	<.0001	logP	0.51	53.5	0.612
HK-p-win	logBa	2.75	47.2	0.0084	logMn	7.5	48.8	<.0001	logP	-2.67	55	0.01
HK-p-sum	logBa	8.81	55	<.0001	logMn	5.8	55	<.0001	logP	-5.95	55	<.0001
JP-p-win	logBa	-0.87	50.6	0.3896	logMn	5.68	51	<.0001	logP	-3.29	51	0.0018
JP-p-sum	logBa	5.87	46.1	<.0001	logMn	8.92	55	<.0001	logP	1.24	55	0.2206
KR-p-win	logBa	1.01	42.6	0.3167	logMn	9.02	56	<.0001	logP	-9.13	56	<.0001
KR-p-sum	logBa	7.55	56	<.0001	logMn	8.31	56	<.0001	logP	-5.77	56	<.0001

Table G-6. Summary statistics for trace element concentrations in Kaohsiung, Busan, Tokyo Bay and Hong Kong. Concentrations were log-transformed prior to analysis.

Tracer	Survey	N	Mean	s	CL	StdDev	s	CL	Minimum	Maximum	exp(log)
logBa	TW-p-win	23	1.83	±	0.03	0.07	±	0.02	1.72	1.96	6.22
logMn	TW-p-win	23	1.79	±	0.13	0.30	±	0.07	1.16	2.31	6.01
logP	TW-p-win	23	3.72	±	0.28	0.65	±	0.15	2.26	4.43	41.24
logBa	TW-p-sum	24	2.23	±	0.02	0.05	±	0.01	2.14	2.32	9.27
logMn	TW-p-sum	24	1.48	±	0.25	0.59	±	0.14	0.25	2.73	4.38
logP	TW-p-sum	24	3.59	±	0.15	0.36	±	0.08	2.96	4.32	36.18
logBa	HK-p-win	24	2.00	±	0.05	0.11	±	0.03	1.84	2.24	7.40
logMn	HK-p-win	24	0.68	±	0.26	0.61	±	0.14	-0.53	1.52	1.97
logP	HK-p-win	24	3.09	±	0.26	0.62	±	0.14	2.10	3.87	21.93
logBa	HK-p-sum	24	2.47	±	0.12	0.28	±	0.06	1.85	2.91	11.87
logMn	HK-p-sum	24	0.60	±	0.43	1.02	±	0.24	-0.87	2.57	1.82
logP	HK-p-sum	24	2.43	±	0.33	0.79	±	0.18	1.55	3.96	11.37
logBa	JP-p-win	20	1.83	±	0.06	0.13	±	0.03	1.62	2.13	6.22
logMn	JP-p-win	20	0.69	±	0.49	1.05	±	0.26	-0.49	2.52	2.00
logP	JP-p-win	20	2.99	±	0.25	0.53	±	0.13	2.51	4.32	19.79
logBa	JP-p-sum	24	2.15	±	0.04	0.10	±	0.02	1.94	2.33	8.54
logMn	JP-p-sum	24	1.54	±	0.41	0.97	±	0.23	0.56	4.20	4.67
logP	JP-p-sum	24	3.74	±	0.29	0.69	±	0.16	2.55	5.19	41.93
logBa	KR-p-win	25	1.95	±	0.13	0.32	±	0.07	1.64	3.24	7.03
logMn	KR-p-win	25	1.31	±	0.28	0.69	±	0.16	-0.12	2.44	3.70
logP	KR-p-win	25	2.33	±	0.12	0.29	±	0.07	1.90	3.16	10.27
logBa	KR-p-sum	25	2.36	±	0.10	0.25	±	0.06	2.09	3.25	10.55
logMn	KR-p-sum	25	1.26	±	0.37	0.90	±	0.21	-0.53	3.38	3.52
logP	KR-p-sum	25	2.66	±	0.21	0.52	±	0.12	2.17	4.62	14.24
logBa	oceanref	33	1.87	±	0.08	0.24	±	0.05	1.31	2.32	6.50
logMn	oceanref	33	-1.23	±	0.45	1.27	±	0.26	-2.81	0.69	0.29
logP	oceanref	33	3.52	±	0.21	0.60	±	0.12	1.99	4.16	33.89

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APPENDIX H. DESCRIPTION OF APPENDICES H–N

The following appendices of raw data have been archived on CD-ROM. Copies of these data can be obtained by request to the technical point of contact (see page iii).

Appendix H. Event Description:

Details of offshore, coastwise and port sampling events undertaken for this project

Appendix I. Transect Physical Data:

Physical data for offshore transects on the U.S. West Coast.

Appendix J. Port Physical Data:

Physical data from semi-annual port surveys in Hong Kong, China; Kaohsiung, Taiwan; Tokyo, Japan; and Busan, Korea.

Appendix K. Transect CDOM Data:

CDOM fluorescence (quinine sulfate equivalent units, QSE) at five wavelength pairs (Excitation/Emission wavelengths: 350/450, 250/450, 265/470 , 320/414, and 370/494 nm) for offshore transects on the U.S. West Coast.

Appendix L. Port CDOM Data:

CDOM fluorescence (quinine sulfate equivalent units, QSE) at five wavelength pairs (Excitation/Emission wavelengths: 350/450, 250/450, 265/470 , 320/414, and 370/494 nm) for semi-annual port surveys in Hong Kong, China; Kaohsiung, Taiwan; Tokyo, Japan; and Busan, Korea.

Appendix M. Transect Metal Data:

Trace element concentrations (μgL^{-1}) for offshore transects on the U.S. West Coast.

Appendix N. Port Metal Data:

Trace element concentrations (μgL^{-1}) for semi-annual port surveys in Hong Kong, China; Kaohsiung, Taiwan; Tokyo, Japan; and Busan, Korea.

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